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THE EFFECT OF STEAM ADDITION ON  
SULPHUR TRIOXIDE FORMATION DURING THE  
COMBUSTION OF LIQUID FUELS.

by

APPUTHURAY SUTHENTHIRAN

Thesis submitted to the Council for National  
Academic Awards in partial fulfilment of the  
requirements for the degree of Master of Philosophy.

The work was carried out at the Energy Centre  
of Middlesex Polytechnic, Bounds Green Road,  
London N11 2NQ.

JANUARY 1989

(i)

ABSTRACT

A study of the kinetics of  $\text{SO}_3$  formation has been undertaken in a liquid fuel fired, non-catalytic quartz tube combustor. The effects of excess air, residence time, gas temperature, and steam injection on the level of  $\text{SO}_3$  produced have been investigated.

A non-catalytic quartz tube combustor was built with the required safety precautions. Provisions for maintaining near isothermal conditions along the tube and also injecting steam into the combustion chamber were made. An electrically heated temperature controlled chamber evaporated the fuel which was mixed with air and passed through a stainless steel sintered disc and a flat flame was produced just outside the disc.

A kinetic study of  $\text{SO}_3$  formation was done with a laminar flame and it was found (a) the excess air, (b) the residence time, (c) the gas temperature all had effects on the formation of  $\text{SO}_3$  in the fluegases. Sulphur trioxide concentration was determined by a chemical wet method.

The effect of steam injection on the formation of Sulphur trioxide was investigated and shown that steam injection in the flame could provide a method of reducing  $\text{SO}_3$  and hence a reduction of corrosion. The maximum amount of  $\text{SO}_3$  reduction was found to be about 14% when steam was injected at 17.5 mm from the origin of the flame.

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CHAPTER 1

1.1.0 GENERAL INTRODUCTION

All conventional fuel oil contains some impurities. These impurities contain various elements as complex organic and inorganic compounds. Notable amounts of Sodium, Sulphur, Vanadium, Nickel, Calcium and Silicon are present in the end residual products (commonly named residual fuel oil) of refined crude oil. The amount of impurities varies widely with the origin of the fuel. Sulphur, Vanadium and Sodium are the major impurities present in fuel oil since they are responsible for many problems in power generating plant. An analysis of some typical Middle Eastern residues is presented in table (1.1).

The physical properties of different petroleum fuels derived from heavy fractions differ only by relatively small amounts, thus the specific gravity, the Carbon to Hydrogen ratio and the calorific value are relatively constant. Major sources of difference, however, include the total Sulphur concentration, the ash content, the viscosity and necessarily the price. The Sulphur content of the fuel may vary from 1 to 5% depending on the origin of the fuel. Vanadium is present in crude oil as a thermally stable substance which is not removed during refining so that all Vanadium present initially in the crude appears in the residual fuel oil. This present work is mainly concerned with the effects of Sulphur in the fuel.

There are three major problems resulting from an increased presence of Sulphur in liquid fuel, viz.

	KUWAIT LONG RESIDUE	QATAR MARINE LONG RESIDUE	IRANIAN HEAVY LONG RESIDUE	ARABIAN HEAVY LONG RESIDUE
VANADIUM ppm	53	26	145	88
NICKEL ppm	12.7	9.7	33.6	26.9
SODIUM ppm	7.7	7.4	7.2	25
SULPHUR %W	4.21	2.77	2.73	4.31
SPECIFIC GRAVITY	0.9336	0.9027	0.9254	0.9514

Table 1.1

METALIC CONTENT OF SOME MIDDLE EAST RESIDUES

REF (4)

- (1) Atmospheric pollution
- (2) Fouling or obstruction of flue passages
- (3) Corrosion of heat exchanger surfaces in boilers and furnaces

(1)

Atmospheric pollution has long been a problem which, with increasing industrialisation, has become more pressing in recent years. Sulphur oxides are now known to be deleterious to all kind of life on earth. An East West agreement to cut sulphur emissions, considered to be the main cause of acid rain in the Industrialised World, took effect in October 1987 after ratification by 16 states according to UN Economic Commission for Europe (43). The requirement for electrical power is projected to increase at an annual rate of 6 per cent during the next 30 years (49). It is generally agreed that the generation and distribution of this quantity of electrical energy will result in unacceptable levels of environmental degradation. The use of Sulphur bearing fuel to generate electrical energy is only one of man's activities contributing to the decline in quality of our air resources. Stack gases from fossil-fueled power plants contain about 1000 to 3000 ppm of  $\text{SO}_2$  depending on the amount of Sulphur in the fuel. Detrimental effects on vegetation, materials and human health are first noticed in areas having 0.03 to 0.04 ppm (annual mean)  $\text{SO}_2$  concentration (49). Many ways of removing  $\text{SO}_2$  from stack gases are being actively investigated. All involving some means of contacting the gas with a substance that removes

SO<sub>2</sub>. The limestone wet scrubbing process is proved to be one of the effective methods and has been installed in sizeable operating power plants.

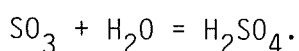
(2)

Fouling or obstruction of flue passages is merely a physical problem. The more troublesome forms of deposits found in power plants consist of metallic oxides, sulphates and chlorides bound together with carbonaceous matter and quite often sulphuric acid. Vanadium in the fuel during combustion forms oxides, the pentoxide V<sub>2</sub>O<sub>5</sub> being the most troublesome with its low fusion temperature influencing slag formation.

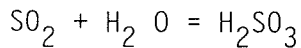
(3)

Problem (3) forms the basis of the experimental work carried out in this project. Corrosion due to flue gas can be generally divided into two main categories, ie, low temperature corrosion and high temperature corrosion.

It is well known that low temperature corrosion is associated with the presence of SO<sub>3</sub> in the flue gases which tends to condense as sulphuric acid on cool surfaces operating below the acid dew point of the flue gases. Hence this is also known as Sulphuric acid corrosion. Sulphur present in the fuel is oxidised to Sulphur dioxide during combustion and some part of it is further oxidised to sulphur trioxide. Sulphur trioxide in the presence of water vapour in the flue gas gives the following reaction to form sulphuric acid:



Below the acid dew point of the flue gases, sulphur dioxide also forms sulphurous acid according to the following reaction and contributes to corrosion:



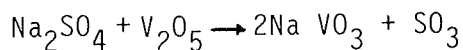
The concentration of the sulphuric acid in the flue gas, which may vary with changes in combustion conditions, has a marked effect on the acid dew point (20). The increase of fuel sulphur increases the  $\text{SO}_3$  formation (14) and hence gives an increase of the acid dew point of the flue gases. An increase in the sulphuric acid vapour concentration from 2-50 vpm for instance raises the dew point of the flue gas from  $121^\circ\text{C}$ - $146^\circ\text{C}$ , if 12% water vapour is present. This means that if the heat exchanger surfaces are not kept above this temperature, sulphuric acid will be deposited. To overcome this phenomenon the temperature in these areas of the plant has to be maintained above the acid dew point of the flue gas. This could mean a waste of valuable heat energy through the chimney stack which results in the loss of vast amounts of revenue, as each degree of temperature increase in the exhaust gas lowers the efficiency of the plant. This can be clearly seen from the following equation for the maximum possible efficiency of a thermal cycle,

$$\eta = \frac{T_1 - T_2}{T_1}$$

where  $T_1$  is the maximum cycle temperature and  $T_2$  the temperature at which heat is rejected, ie, the flue gas exit temperature. The efficiency of the plant will be at a maximum when  $T_2$  is a minimum. This temperature, therefore, has to be maintained

above the acid dew point to prevent condensation and thus fouling of the plant due to corrosion. Hence it is desirable to reduce the dew point temperature to enable the flue gas to leave the plant at a lower temperature and hence give a higher plant efficiency.

High temperature corrosion is mainly caused by inorganic substances such as Vanadium and Sodium and Sulphur. This corrosion occurs when metal surfaces are exposed to the flue gases at about 650°C. At these elevated temperatures even high grade steels are attacked and corrosion becomes a serious problem. During combustion, Vanadium present in the fuel is converted to various vanadium oxides. In the presence of other residues such as Sodium Sulphate at a temperature of 630°C and above Vanadium pentoxide ( $V_2O_5$ ) gives the following reaction.



In case of superheater tubes of oil fired boilers, high temperature corrosion is a major problem only if the operating temperatures are above the sintering or softening temperature of ash deposits. Corrosion then occurs through the fluxing action of the Vanadates. High temperature corrosion is, however, a more serious problem in the case of gas turbine blades.

To limit the amount of the acid deposits it would seem evident that a reduction in the amount of  $SO_3$  formed is necessary. This could be accomplished by reducing the sulphur content of the fuel. Most of the sulphur in the fuel is eliminated from the lighter fuels at the refining stage. Refining



a completely sulphur free fuel is uneconomical and impractical with present technology. Hence the use of high sulphur fuel in power plants may be necessary on cost grounds. The relative lack of profitability in recent history and, therefore, the deferment of new installations in the oil industry indicates the obligation on most industries to use high sulphur fuels wherever applications merit.

The most attractive solution to this major problem is of course to eliminate sulphur from oil fuels. As has been seen, however, this is impractical and not economically feasible. Methods must be adopted for reducing the formation of  $\text{SO}_3$  by either modification of the combustion process or in some way to remove sulphur oxides from the flue gases. The latter is the more usual in power plants and flue gas desulphurisation plant is well established and effective, but rather expensive.

The reduction of  $\text{SO}_3$  formation in the combustion process by the use of additives, either in the fuel or combustion zone, is a well tried technique. Several chemical additives have been used in various parts of the boiler and have met with varying degrees of success. These include Ammonia, Dolomite, Magnesium carbonate, Magnesium hydroxide, Magnesium oxides, Carbon monoxide, Mineral silicates, Organic silicon compounds and Silica. Magnesium hydroxide was found to be the most effective additive (48). Work has been carried out by S A Kahn at Middlesex Polytechnic by using various additives on the suppression of  $\text{SO}_3$  to this effect.

In order to introduce additives an understanding of the mechanism of formation of  $\text{SO}_3$  in the combustion system is vital. The basic reaction between sulphur and oxygen in combustion is that which produces  $\text{SO}_2$ , the  $\text{SO}_3$  is formed by subsidiary reactions. The overall reaction mechanisms involved in forming  $\text{SO}_3$  are complex and have been reviewed by Cullis and Mulcahy (19). Obviously, a reaction from  $\text{SO}_2$  to  $\text{SO}_3$  needs oxygen for it to be initiated and thus a reduction of the available oxygen in the flue gas would seem to be a probable solution. Investigations by earlier workers show that limiting the excess oxygen by combustion control reduces low temperature corrosion. It has been stated by Kirov (21) that when the free oxygen in the combustion gases was reduced to one per cent or less, the  $\text{SO}_3$  concentration decreased from 20-40 ppm to below 7 ppm in a boiler at the Marchwood power station. A great deal of work has been carried out by research workers to suppress the formation of  $\text{SO}_3$  in flue gases and it appears that the problem is not yet totally solved.

Steam injection and water addition have been used in the suppression of  $\text{NO}_x$  formation and have proved effective in reducing  $\text{NO}_x$  by more than 80 percent (15, 16, 41, 42). The complete mechanism of the formation of oxides of nitrogen in flames is not fully understood (40). Whatever the mechanism of formation of  $\text{NO}_x$  the following statements hold true:

- (1) The  $\text{NO}_x$  level is strongly increased by a longer residence time. (15, 40.)
- (2) The  $\text{NO}_x$  level is strongly increased at high temperatures (those existing in flames). (15, 40.)
- (3) The  $\text{NO}_x$  level is increased by higher oxygen concentration. (15, 40.)

It is also clear from the vast amount of literature available that the above statements hold true in the case of  $\text{SO}_x$  formation too. Hence, it might be expected that the addition of steam or water in the combustion system will reduce  $\text{SO}_x$  too. However, it appears that no work has been done to the use of steam or water as an additive to suppress  $\text{SO}_3$  formation in combustion systems. It has been mentioned by Melton, Lestz, Quillian and Rambee (30) that there is a probability that oxides of Sulphur ( $\text{SO}_x$ ) might be removed from an engine exhaust during operation with water injection. If so, this could make fuels with relatively high sulphur content look attractive, at least, perhaps for stationary applications. Hence, it was decided to use steam injection in the combustion process to investigate the effect of it on the formation of  $\text{SO}_3$ . In the present work stress is laid on a kinetic study of  $\text{SO}_3$  formation in a non-catalytic environment and particularly the effect of steam injection at various positions in the flame.

The objectives of this work are:-

- (a) A kinetic study of  $\text{SO}_3$  formation in a non-catalytic environment.
- (b) To investigate the effect of steam injection into the flame zone on the formation of  $\text{SO}_3$ .

## CHAPTER 2

### 2.1 LITERATURE SURVEY

#### 2.1.0 INTRODUCTION

Sulphur in the form of organic compounds generally accounts for several per cent, by weight, of the fuel burnt in power stations and other large industrial plant. The most common effects of its combustion are pollution by sulphur oxides emitted to the atmosphere and corrosion of plants by sulphuric acid. It is sufficient to say that if a fuel oil containing sulphur is burnt in a combustion chamber then the sulphur in the fuel will be oxidised during the combustion process. Altogether some six oxides of sulphur have been characterised (51). Of these only sulphur dioxide and sulphur trioxide are stable both under normal atmospheric conditions and at higher temperatures. The predominant sulphur containing product formed by the combustion of sulphur compounds is sulphur dioxide ( $\text{SO}_2$ ). Even when oxygen is largely in excess, sulphur trioxide ( $\text{SO}_3$ ) is hardly found in amounts greater than a few per cent of the  $\text{SO}_2$ . Typically the ratio of  $\text{SO}_2$  to  $\text{SO}_3$  in combustion gases ranges from 20:1 to 80:1. Although,  $\text{SO}_3$  concentrations are relatively small compared to that of  $\text{SO}_2$ , its presence has profound effects on thermal plant operation. In most circumstances  $\text{SO}_3$  appears in combustion products at room temperatures as sulphuric acid.

#### 2.1.1 PRACTICAL EFFECTS OF $\text{SO}_x$

The appearance of sulphur in fossil fuels creates a wide variety of problems for industry and the atmosphere. These can be categorised into two main groups:

(a)

The atmosphere may be polluted by gaseous sulphur compounds emitted by combustion plant. These are known to be  $\text{SO}_2$  and smaller amounts of  $\text{SO}_3$ .

The emission of  $\text{SO}_2$  (in this paragraph  $\text{SO}_2$  designates the sulphur oxides in stack gases, ie,  $\text{SO}_2$  plus 1 to 2 per cent  $\text{SO}_3$ ) from combustion of sulphur bearing coal and oil, primarily for the generation of electrical energy, is second only to the emission of pollutants from internal combustion engines in quantity of pollutants discharged to the national air environment. The substitution of low-sulphur fuels, the only presently available method for reducing  $\text{SO}_2$  emissions, is restricted by the limited availability of natural gas, low-sulphur oil and low sulphur coal. More rapid expansion of the application of nuclear energy is constrained by engineering and economic problems, in addition to siting problems that are of growing concern to all planners of major electricity generating installations. Therefore, the reduction of  $\text{SO}_2$  emission from stationary combustion sources will depend very largely on the development, demonstration and application of a combination of technologies designed to prevent the sulphur in coal and petroleum products from reaching the atmosphere through the combustion processes. Concern on  $\text{SO}_2$  emitted to the atmosphere from electricity generating plants came to great attention because: (1) This is the largest man-made source of sulphur oxides: (2) it is widely dispersed nationally, but is largely concentrated in or near urban centres: (3) it is growing at about 6 per cent per year, (4) it is intimately related to

the national and international flow of energy resources:

(5) it is important to regional economic development, and

(6) it is critical to continued national well-being, security and economic growth.

Stack gases from fossil-fueled power plant contain about 1000 to 3000 ppm of  $\text{SO}_2$  depending on the amount of sulphur in the fuel. Detrimental effects on vegetation, materials and human health are first noticed in areas having 0.03 to 0.04 ppm (annual mean)  $\text{SO}_2$  concentration. Thus a  $10^5$  fold dilution or reduction in concentration is required, on the average, by the time the  $\text{SO}_2$  reaches ground level (49).

(b)

The plant may corrode or the passage of the combustion gases fouled by solid or liquid sulphur compounds.

With regard to the corrosion problem, it is well known that all the sulphur in the fuel is converted to  $\text{SO}_2$  during combustion under normal excess oxygen conditions. Sulphur trioxide produced from this combustion usually amounts to 1 to 2 per cent of the sulphur dioxide present in the flue gases (21, 38). The conversion of  $\text{SO}_2$  to  $\text{SO}_3$  is the key to corrosion problems in boilers. The general facts concerning the occurrence of corrosion and deposit formation have been widely investigated by Johnson and Littler (22).

Metal corrosion leads to a loss of capital associated with the malfunctioning of certain parts of the plant (ie boiler tubes, air heaters, economizers) after a very short lifetime. In many cases, the result has been the need to

replace major parts of equipment after a few months of operation, when lifetimes of 5 to 10 years would be expected. In general it is not possible to specify fuels of low sulphur content for large boiler plants because the cheaper residual fuels for which these boiler plants are designed inherently contain more sulphur compounds than other lighter petroleum oils.

The corrosion due to flue gas can be generally divided into two main categories:

- (i) High temperature corrosion.
- (ii) Low temperature corrosion.

High temperature corrosion is experienced mainly with residual fuel oils, and it is primarily due to the presence of Vanadium, Sodium and Sulphur compounds in the fuel. During combustion such compounds give rise to complex low melting point materials which are deposited on heat transfer surfaces and supporting structures. Such deposits trap large amounts of ash which would not otherwise adhere to the surfaces. The presence of deposits not only impedes heat transfer, but also causes corrosion. These considerations restrict steam superheat temperature and hence the thermal efficiency of the plant. High temperature corrosion occurs at temperatures above 600°C and at these temperatures even high grade steels are affected.

Low temperature corrosion is mainly sulphuric acid corrosion and occurs by aqueous sulphuric acid precipitated on cooler surfaces, mostly in economisers, air heaters, flue stacks and other parts where the temperature of the metal parts is near and below the acid dew point (approximately 130°C) of the



combustion gases. Fuel oil may contain between one and 5 per cent of sulphur. During combustion the sulphur in the fuel is mostly converted to sulphur dioxide, with an additional 1-2% of sulphur trioxide. The amount of  $\text{SO}_3$  is strongly dependent on the amount of excess oxygen present in the combustion flame. Investigations by earlier workers show that limiting the excess oxygen by combustion control reduces low temperature corrosion. Dry  $\text{SO}_3$  is non-corrosive but condensed sulphuric acid is highly corrosive. A lower concentration of  $\text{SO}_3$  provides a lower acid dew point and less sulphuric acid.



### 2.1.2 RELATIONSHIP OF $\text{SO}_3$ WITH ACID DEW POINT

It is widely recognized that serious difficulties are brought about by acid deposits in the air heaters and economizers of boiler plants due to abnormally high dew point temperatures of the flue gases and that the elevation of the dew point is a result of the gases containing an excessive amount of sulphur trioxide. A lower concentration of  $\text{SO}_3$  provides a lower acid dew point, and less sulphuric acid. This phenomenon has been explained by Exley (18), Banchero and Verhoff (23) in great detail. By burning different fuels with varying sulphur contents Rendle and Wilsdon (28) showed that the  $\text{SO}_3$  content of the flue gas increases with an increase of sulphur content in the fuel. It was also shown that for fuels of sulphur content from one per cent to 5 per cent, by weight, the dew point rises by approximately  $4^\circ\text{C}$  for each one per cent weight rise in sulphur content. Thus to bring about an appreciable reduction in the dew point by the desulphurization or dilution of high-sulphur fuels, it would be necessary to reduce the sulphur content to below 0.5 per cent by weight. Fig 2.1 shows the relationship of dew points of fuel combustion gases to the sulphur content of the fuel.

It has been estimated that in the combustion of one ton of oil per hour in a boiler plant, enough sulphuric acid may be formed to dissolve one ton of steel every 1,000 hours (21). However, in practice most of the sulphur oxides pass through the plant into the atmosphere. As a step to avoiding acid condensation phenomenon, and the operational difficulties to

which it can lead, it is important to have an accurate knowledge of acid dew point (ie, the highest temperature at which condensation can occur). Direct methods for dew point determination rely on the detection of the initial formation of a liquid phase upon a cold surface. The results of a number of such experiments carried out by other workers are given by Halstead and Talbot (20). It has been found that flue gas containing the average oil plant concentration of water vapour (11 Vol%) possess an acid dew point of  $125^{\circ}\text{C}$  for an  $\text{H}_2\text{SO}_4$  vapour phase concentration of 5 vpm, rising to  $137^{\circ}\text{C}$  for 20 vpm  $\text{H}_2\text{SO}_4$  and  $152^{\circ}\text{C}$  for 100 vpm (20). Variation in the water vapour content of the flue gases have only a small effect on the acid dew points.

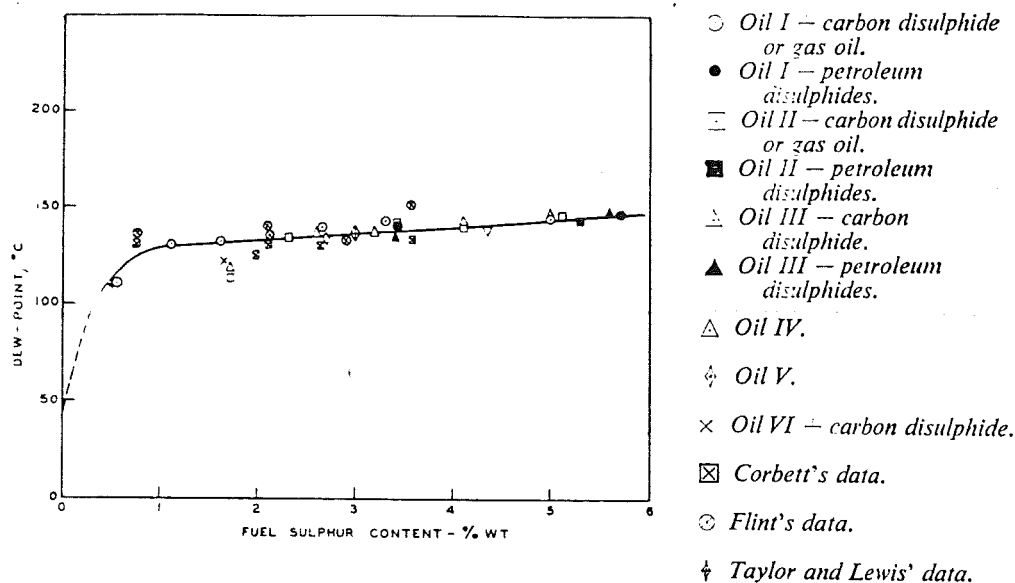


FIG 2.1 Variation of measured dew-points of fuel combustion gases with sulphur content of fuel. All data refer to 25% excess air for combustion (28).

### 2.1.3 SO<sub>3</sub> FORMATION IN COMBUSTION DEVICES

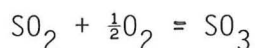
A number of theories have been postulated to explain the mechanism of SO<sub>3</sub> formation. The two most important of these are (a) atomic oxygen theory, also known as the flame theory and (b) the catalytic theory. The former postulates that SO<sub>3</sub> is formed in the flame by a combination of SO<sub>2</sub> with atomic oxygen present in the flame, ie:



where M is a third body (eg. H<sub>2</sub>O).

This theory was introduced by Dooley and Whittingham in 1946 (1) and Gaydon and Whittingham in 1947 (2). Hedley (7,8) and Ahmed (9) supported this theory with results obtained from investigations on laminar diffusion flames and premixed laminar flames, respectively.

The catalytic theory postulates that SO<sub>3</sub> is formed by catalytic oxidation, on surfaces in the path of the combustion gases.



This theory can be attributed to Harlow (3). Some of the SO<sub>2</sub> present can be oxidised to SO<sub>3</sub> as the flue gases pass over metal surfaces operating at temperatures above about 435°C. The catalyst in this oxidation could be Ferric Oxide. The work of Squires (10) and Burdette (11) supported the catalytic theory for the formation of SO<sub>3</sub> in combustion systems. The fundamental difference between the two theories is that the second involves consideration of SO<sub>2</sub> oxidation with molecular oxygen at catalytic surfaces while the first proposes that SO<sub>3</sub> formation takes place by a homogeneous

reaction with an oxidising flame species. The formation of  $\text{SO}_3$  by heterogeneous catalysis is historically well known, however, being the basis of the contact process for the industrial manufacture of sulphuric acid.

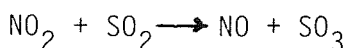
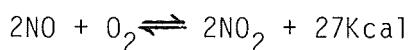
It has been shown that whatever the mechanism, a reduction in excess air will lead to a reduction in the percentage conversion of  $\text{SO}_2$  to  $\text{SO}_3$ . For example, no Sulphur trioxide is found in smokey flames. Crumbly and Fletcher (5) performed tests with a small oil fired boiler burning kerosene doped with carbondisulphide to assess the effects of sulphur content, flame temperature, excess air and flame types on  $\text{SO}_3$  formation. They found that increases in sulphur content, flame temperature and excess air all led to an increased percentage of  $\text{SO}_2$  being oxidised to  $\text{SO}_3$ . Laxton (6) obtained results in some agreement with Crumbly and Fletcher, for he found that the percentage oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  increased with sulphur content of the fuel oil. Rendel and Wilson (28) showed that by burning different fuels with varying sulphur contents, the  $\text{SO}_3$  content in the flue gases increased with increase of sulphur in the fuel. Hedley (7) showed that considerable quantities of  $\text{SO}_3$  could be found in the flames produced in a laboratory scale apparatus. The figures produced were much in excess of the concentrations found from thermodynamic calculations. By considering the equation

$$\text{SO}_2 + \frac{1}{2}\text{O}_2 \xrightarrow{K_p} \text{SO}_3$$

and by knowing the equilibrium constant  $K_p$ , the maximum theoretical yield of  $\text{SO}_3$  at a specific temperature can be calculated. The variation of  $K_p$  with temperature has been

given in table form by Macfarlane (52) and has been used in the thermodynamic calculation of the  $\text{SO}_3$  yield. This calculation is shown in appendix (VI), Hedley concluded from the results of his tests that the majority of the  $\text{SO}_3$  found in combustion gases originates in the combustion chamber. Nettleton and Stirling (12) carried out a series of experiments in an alumina reactor tube. The oxidation of sulphur dioxide was studied in preheated and premixed carbon monoxide - nitrogen - oxygen and methane - nitrogen oxygen flames. Their results showed a marked increase in the oxidation of sulphur dioxide in the presence of a flame and the suppression of the oxidation of sulphur dioxide by atomic oxygen scavengers substantiated the flame theory. It has also been observed that when mixtures of sulphur dioxide and oxygen are passed through a quartz tube in furnaces at above  $1000^\circ\text{C}$ , no conversion to sulphur trioxide takes place, but if a little benzene was added so that flame was produced, sulphur trioxide is immediately formed which implies that atomic oxygen is produced by the flame and hence agreeing with the flame theory. Merryman and Levy (38) investigated  $\text{SO}_3$  flame chemistry with  $\text{H}_2\text{S}$  and  $\text{COS}$  flames and concluded that the formation of  $\text{SO}_3$  occurred via a three body reaction involving  $\text{SO}_2$  and  $\text{O}$  atoms. It was also found that the reaction is pressure dependent producing more  $\text{SO}_3$  at higher pressures. Halstead (17) also states that some  $\text{SO}_3$  will form downstream of the flame due to the presence of gaseous (ie nitrogen oxides) and solid (ie iron oxide) catalysts. Hedley has also stated that Nitrogen oxides present in the combustion

gases could be regarded as homogeneous catalysts in the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  due to the following reaction:



Levy and Merryman (13, 38) obtained  $\text{SO}_3$  profiles just above a flat premixed hydrogen sulphide and carbonyl sulphide flames, and showed that  $\text{SO}_3$  formation dropped dramatically as the probes used to assess the  $\text{SO}_3$  formation were progressively moved away from the flame. Thus they concluded that the  $\text{SO}_3$  was formed only from the reaction of  $\text{SO}_2$  with atomic oxygen existing in the flame. These results also showed that an increase in the total pressure in a given flame results in increased  $\text{SO}_3$  formation in the flame.

The observation that air entering the combustion gases downstream of the flame does not oxidize sulphur dioxide shows that in these circumstances the sulphur trioxide detected was produced entirely in the flame.

The effect of sulphur content in the fuel on  $\text{SO}_3$  emission operating with excess combustion air is shown in Fig 2.2

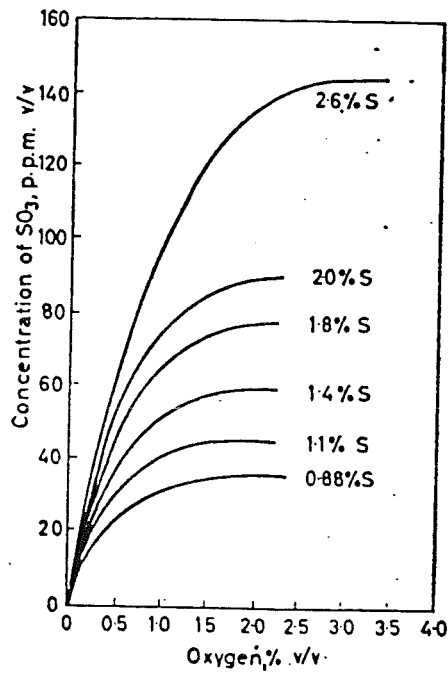


FIG 2.2 Measurements on the variation of  $\text{SO}_3$  in flue gas with oxygen level and sulphur in the fuel (6).

An increase in fuel sulphur brings about an increase in  $\text{SO}_3$  (27, 28) emitted from the system. This has been corroborated in FIG 2.3 where the variation of the dew point temperature of the burnt gas with excess air was measured. The dew point is related approximately linearly to the sulphur trioxide concentration in the range 40-120°C (27).

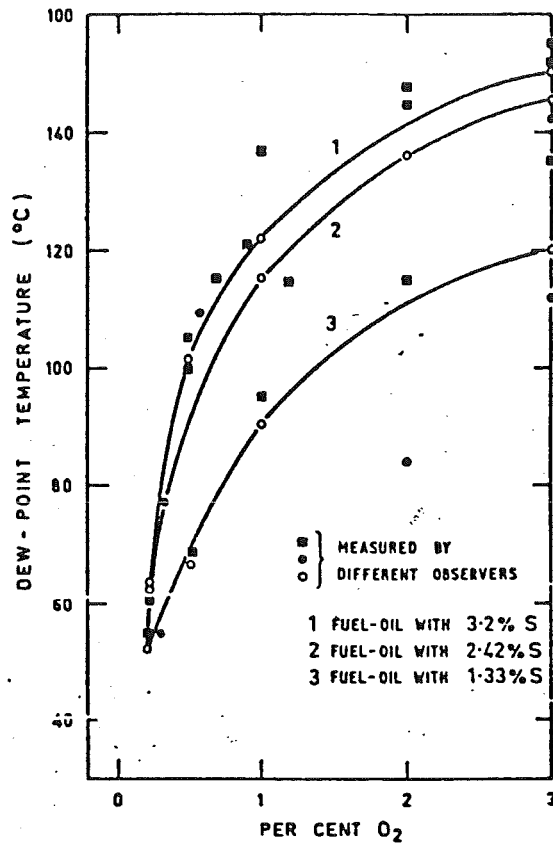


FIG 2.3 Effect of excess air on the sulphuric acid dew point in an oil fired boiler (27).

By burning kerosene +3.4%S(wt) and diesel, ie gas oil +2.5%S(wt) in a premixed laminar flame combustor Ahmed and Zaczek (9) showed that the  $\text{SO}_3$  formation increases with the increase of  $\text{O}_2$  up to about 4.5% excess oxygen FIG 2.4. Thereafter the increase of excess  $\text{O}_2$  brought about a reduction in the  $\text{SO}_3$  concentration. This could be due to the dilution effect of  $\text{SO}_3$  by excess air.



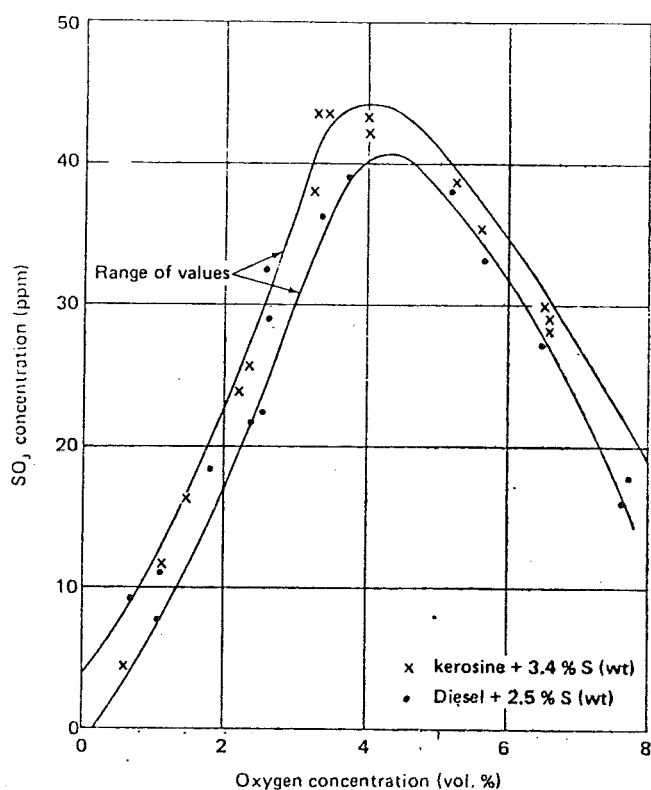


FIG 2.4 Effect of excess oxygen on the formation of SO<sub>3</sub> for kerosene and diesel fuel.

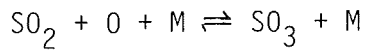
Ref. Ahmed and Zaczek (9).

A very extensive review on sulphur containing compounds in combustion systems has been published by Cullis and Mulcay (19). Their review deals with that part of field which is relevant to the kinetic behaviour of sulphur compounds which either undergo combustion themselves or may be present in other gaseous combustion systems. Initially an overall kinetic behaviour observed in the combustion of gaseous sulphur compounds is described to review the state of knowledge regarding the elementary reactions which may play a part during combustion of sulphur containing species. In the last

part of the review an attempt is made to show how information regarding the kinetics of the reactions of sulphur compounds, derived from laboratory experiments is useful in interpreting the behaviours of sulphur in practical combustion systems.

#### 2.1.4 KINETICS OF THE SYSTEM $\text{SO}_2/\text{O}/\text{SO}_3$

The most likely reaction responsible for the major source of sulphur trioxide formation in practical combustion systems is:



where M is a third body (eg  $\text{H}_2\text{O}$ ).

Hedley (8) showed that in flame gases, the  $\text{SO}_3$  concentration normally exceeds the level given by theoretical equilibrium considerations, while in the cooled gases the  $\text{SO}_3$  levels are below equilibrium. FIG 2.5 presents both experimental and theoretical concentrations of  $\text{SO}_3$ .

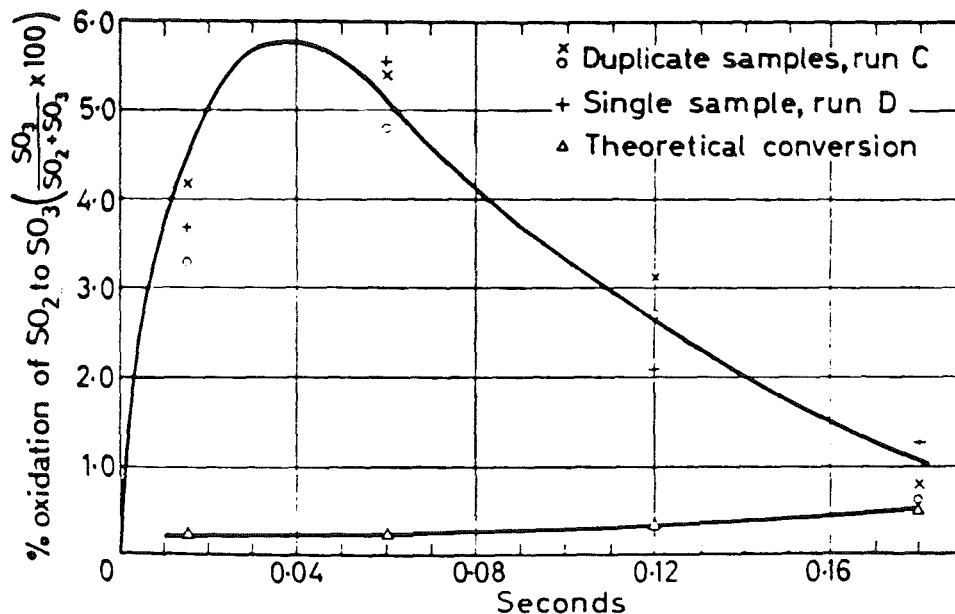
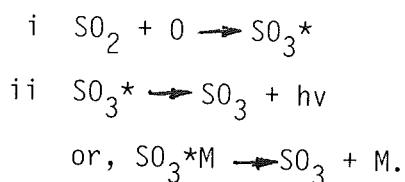


FIG 2.5 Variation of % oxidation of  $\text{SO}_2$  with residence time (8).

The explanation given by Hedley for  $\text{SO}_3$  behaviour during its formation was based upon a mechanism by which  $\text{SO}_3$  was formed by the collision between an  $\text{SO}_2$  molecule and atomic oxygen. When a  $\text{SO}_2$  molecule and an oxygen atom collide in absence of a third body M, it is possible that an activated molecule of

$\text{SO}_3^*$  (molecule with excess energy which is unstable, symbolised by  $\text{SO}_3^*$ ) could be formed. This excess energy could be removed by radiation or by later collisions with a third body thus:



It is also evident from FIG 2.5 that oxidation of  $\text{SO}_2$  is dependent upon the residence time. Work by the author and other workers (45) shows that if the gas temperature along the tube is elevated to a near isothermal condition then the amount of  $\text{SO}_3$  increases. Work done earlier by Hedley (7) and Ahmed (9) show that as the gas temperature was decreasing with increase of residence time the  $\text{SO}_3$  concentration was decreasing too after reaching a maximum, where, as the author and other workers (45) found, when the temperature was maintained fairly constant the  $\text{SO}_3$  concentration increased with increase of residence time. This increase of  $\text{SO}_3$  is explained as due to the increase of atomic oxygen because of the increase of temperature. Hence, atomic oxygen is a more likely source of increasing the  $\text{SO}_3$  in combustion system. As can be seen from experimental data given by Barret and others (14)  $\text{SO}_3$  is formed only where there is excess oxygen present. Production of  $\text{SO}_3$  is largely determined by the first few per cent excess of oxygen, which is evident from FIG 2.6.

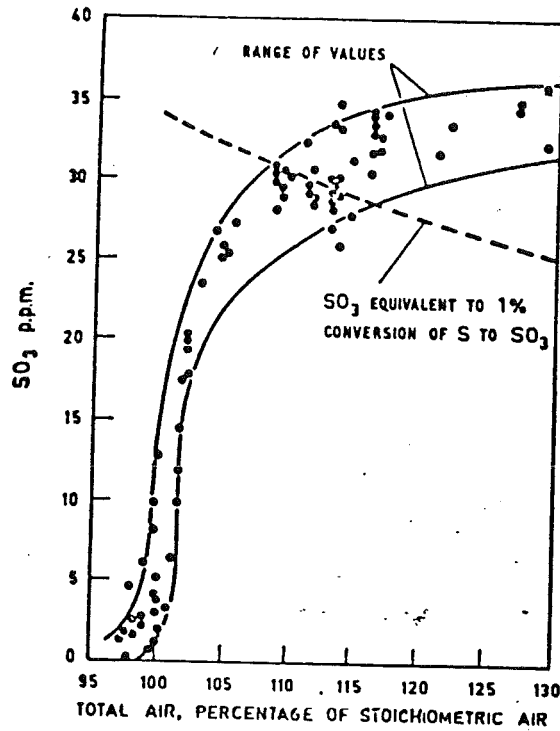
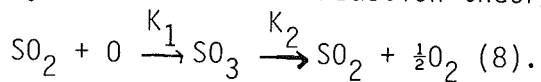


FIG 2.6 Measurement of the effect of excess air on the formation of sulphur trioxide in a Hydrocarbon flame, ref (14).

The SO<sub>2</sub> oxidation seems to be carried out by the oxygen atoms. Since SO<sub>2</sub> is an easily oxidizable substance at flame conditions, one could expect SO<sub>2</sub> to react rapidly with oxygen atoms to form SO<sub>3</sub>. The SO<sub>3</sub> thus formed is of a transient nature and is well above equilibrium concentrations and, therefore, dissociation begins. The theory can be represented by the consecutive reaction theory.



where  $k_1$  and  $K_2$  are the specific reaction rate constants for the individual reactions. Assuming the reactions above are two consecutive first order reactions, the kinetics of SO<sub>3</sub> formation is given by:

$$[SO_3] = [a] \frac{K_1}{K_2 - K_1} [e^{-K_1 t} - e^{-K_2 t}]$$

where  $[SO_3]$ : concentration of  $SO_3$  after a time  $t$

$[a]$  : initial concentration of atomic oxygen.

A mathematical method derived by Lanczos was used by Ahmed

(9) and the following values were obtained for  $a$ ,  $K_1$  and  $K_2$ .

$$[a] = 118 \text{ ppm} \quad K_1 = 11.8 \text{ s}^{-1} \quad K_2 = 1.24 \text{ s}^{-1}$$

The above values for the specific reaction rate constants

show the rate of formation of  $SO_3$  is approximately eight times the rate of its dissociation.

### 2.1.5 ACID DEW POINT AND ADDITIVES

The presence of sulphur in fuel oils causes a considerable rise in the dew point of the flue gases. In order to avoid corrosion of heat-exchanger surfaces, it is the general practice to maintain these at temperatures above the acid dew-point, with a consequent loss of thermal efficiency over that obtainable in the absence of sulphur. The effect of the sulphur content of fuel oils on the dew points and  $\text{SO}_3$  content of the combustion gases has been investigated by a number of workers. It has been found that at 25 per cent excess air the dew point of the flue gas from a sulphur-free fuel is  $45^{\circ}\text{C}$ ; while for a fuel of one per cent weight sulphur content, the dew point is about  $130^{\circ}\text{C}$ . In the range of fuel sulphur content from one to 5 per cent weight the dew point increases by approximately  $4^{\circ}\text{C}$  for each one per cent weight rise in sulphur content (28).

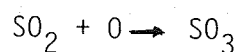
The use of a variety of materials for depressing the acid dew point of flue gases has been described in technical literature in recent years. These materials fall into three main classes, depending on the mechanism by which the  $\text{SO}_3$  is removed.

(a)

Materials which physically adsorb  $\text{SO}_3$  such as silica or carbon. For efficient adsorption the materials must be introduced in an activated, finely divided form as smokes or dusts, so that maximum specific surface area is offered to the gases.

(b)

Materials which combine preferentially with the atomic oxygen present in the flame zone or which promote recombination of the oxygen atoms with consequent inhibition of the reaction



Again the efficiency of the process depends on the available surface area of the solid.

(c)

Materials which combine with  $\text{SO}_3$  chemically to form non-corrosive compounds, which are carried away by combustion gases. Compounds of Magnesium and Zinc fall into this category. For efficient contacting with the  $\text{SO}_3$  a high active surface to volume ratio is again necessary.

Materials from each of these classes have been assessed in an experimental furnace by Rendle and Wilsdon (28). Most of the materials which were successful in lowering the acid dew point belonged to class (c).

If flue gas additives are to be accepted as part of normal power station equipment then a number of conditions should be fulfilled:

- (i) The chemicals to be used should be simple and their action explained and understood in scientific terms.



- (ii) There must be no significant adverse side effects on plant or the environment which will outweigh the benefits.
- (iii) Reliable injection equipment must be available. This implies the design and development of equipment in the knowledge of the optimum properties required of the particles for the additive to be most effective.
- (iv) The additive cost when compared with fuel cost must be low and there should be some scope for recovering part of the additive cost, eg, reduce corrosion or a lower back-end temperature.

It has been mentioned that fuel dispersed additives introduced more operational difficulties than simple back-end powder addition and were generally more expensive (54).

A number of materials such as silicas, carbon, oil soluble metallic soaps, metallic oxides, Nitrogenous materials, oxides of Magnesium, Zinc dust, Dolomite, Ammonia, have been tried as flue gas dew point depressants when burning residual fuel oil (21, 28). Ammonia and Magnesium compounds have proved to be most successful as additive materials (28, 48).

### 2.1.6 MEASUREMENT TECHNIQUES OF $\text{SO}_3$ IN COMBUSTION GASES

A number of experimental methods (31, 32, 33, 36, 55, 56) have been published in order to estimate the  $\text{SO}_3$  in combustion gases. Two methods are available to determine the  $\text{SO}_3$  in combustion gases, the Condensation method and dew point method.

Corbett (31) developed a satisfactory chemical procedure for determining  $\text{SO}_3$  by condensation method. This condensation method was subsequently modified by Fielder (32) and improved to involve absorption of the  $\text{SO}_3$  in isopropyl solution which was analysed by either a gravimetric or turbidimetric procedure. Another design of condensation sampling equipment has been developed by Goksayer and Ross (33). The method presented by the latter authors appeared to be simple and reproducible. Dooley and Whittingham (1) developed and used methods for measuring acid dew points. It has been shown that sulphuric acid in flue gases can be accurately determined by the condensation method and the precision of the method in the range of concentration normally is  $\pm 0.3$  ppm (50). Salooja (34) has discussed the errors in the various methods for the determination of  $\text{SO}_2$  to  $\text{SO}_3$ .

Currently there are instruments used by C.E.G.B. to sample and monitor  $\text{SO}_3$  continuously. These instruments were developed at MEL and now marketed by Severn Science. A comprehensive account of the principles and operating features of these instruments has been given by Jackson (36).

## 2.2 NO<sub>x</sub> FORMATION AND EMISSION

### 2.2.0 INTRODUCTION:

A detailed study of the mechanisms of NO<sub>x</sub> formation is beyond the domain of this research study, however, a brief outline of the mechanism of NO<sub>x</sub> formation is given here because the formation of NO<sub>x</sub> and SO<sub>x</sub> depends mainly on residence time, temperature and atomic oxygen. Hence, a method effective in suppressing NO<sub>x</sub>, such as water or steam injection, could be adopted to suppress SO<sub>x</sub> too. Therefore, a study of NO<sub>x</sub> formation and its reduction by steam or water addition could give some understanding of how the reduction takes place.

### 2.2.1 NO<sub>x</sub> FORMATION

There are several oxides of nitrogen but in combustion processes only nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) are formed in sufficient quantity to be important. The term NO<sub>x</sub> in this text is used to denote the sum of NO and NO<sub>2</sub> without specifying the relative amount of each. The other oxides of nitrogen are not considered.

When fuel is burnt in air oxides of nitrogen are formed, partly by the combustion of atmospheric nitrogen and oxygen at high temperatures and partly by the oxidation of nitrogen in the fuel. The degree of eventual formation of NO<sub>x</sub> within a given combustion system depends on combustion conditions such as the residence time, temperature and atomic oxygen content (15). Emission from various types of large boiler using fossil fuels range from 50 to 1500 ppm (29).

One of the most important causes of the notorious photo-chemical smogs that affect large areas of the west coast of the USA is the emission of nitrogen oxides to the atmosphere. It has been established that motor vehicles are one of the major contributors to air pollution particularly by producing unburned hydrocarbons and nitrogen oxides (40). Power generating plants too, pollute the atmosphere by emitting nitrogen oxides.

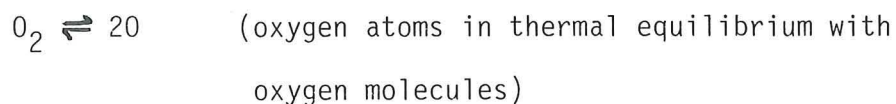
### 2.2.2 REACTION MECHANISM OF $\text{NO}_x$ FORMATION

Generally speaking the reaction mechanism of NO formation depends on the nature of the reactant, the nitrogen containing compound, which may be molecular nitrogen from the atmosphere or organic molecules containing N-H, N-C, N=C or  $\text{N}\equiv\text{C}$  bonds from fuel, and on the nature of the available coreactants. The following mechanisms are distinguished in the formation of  $\text{NO}_x$ :

- (a) The thermal  $\text{NO}_x$  formation mechanism.
- (b) The fuel  $\text{NO}_x$  formation mechanism.
- (c) The prompt  $\text{NO}_x$  formation mechanism.

(a)

The thermal  $\text{NO}_x$  is formed according to the following reactions proposed by Zeldovich (57):



As far as thermal  $\text{NO}_x$  formation is concerned the important parameter to be controlled is in the first place temperature and in the second place the oxygen atom concentration.

(b)

Fuel  $\text{NO}_x$  is formed from the combustion of organic nitrogen compounds present in the fuel. The formation rate of  $\text{NO}_x$  from this mechanism is much faster than the thermal  $\text{NO}_x$  formation. It has been said that the formation of  $\text{NO}_x$  mainly takes place in the flame front and the very early flame zone. The relative value of the maximum  $\text{NO}_x$  concentration, ie, the  $\text{NO}_x$  yield depends on the initial fuel nitrogen content and decreases with increasing equivalence ratio, where

$$\text{equivalence ratio } \phi = \frac{\text{stoichiometric air/fuel ratio}}{\text{Actual air/fuel ratio}}$$

(c)

Prompt- $\text{NO}_x$  was classified in order to explain a very fast  $\text{NO}_x$  formation in the visible flame zone of fuel rich hydrocarbon flames, originating from molecular nitrogen (59). The prompt  $\text{NO}_x$  formation is due to the reaction of hydrocarbon fragments with nitrogen (42). This form of  $\text{NO}_x$  formation is enhanced when the equivalence ratio is high. Owing to the fact that nitrogen molecules need some carbon containing radicals as coreactants, their existence is evidently restricted to the early flame zone.

Calculations by Fenimore (58) to determine how significant is prompt- $\text{NO}_x$  compared with thermal  $\text{NO}_x$ , indicate that for a combustor with a mean residence time of 2 ms and with an adiabatic stoichiometric flame using kerosene and air, the combustor would emit 178 ppm NO of which 27% is prompt- $\text{NO}_x$ .

Whatever the mechanism of formation of NO the following statements hold true (40).

1. The NO level is strongly increased at high temperatures (those existing in flames).
2. The NO level is strongly increased by a longer residence time.
3. The NO level is increased by a higher oxygen concentration (atomic oxygen content).
4. The principal oxide of nitrogen in a combustor is NO, this being kinetically favoured over all others.

Nitrogen dioxide is considered to be the more important with respect to air pollution since it is the cause of photo-chemical smog and if exceeding 5 ppm is a serious hazard to human health. Under certain operating conditions,  $\text{NO}_2$  constitutes the bulk of  $\text{NO}_x$  produced by some gas turbines, diesel and spark ignition engines (61).

### 2.2.3 CONTROL METHODS

Substantial analytical and experimental background already exists on the reduction of nitric oxides from gas turbine engines. This data provided a basis on which to outline the methods to reduce the amount of these oxides.

There are four fundamental approaches for controlling  $\text{NO}_x$  emissions from gas turbine engines:

(a)

To modify the engine design (primary and combustor section) in order to provide temperature, residence time, oxygen concentration, and air to fuel ratio less favourable to the formation of nitrogen oxides. The various combustor modifications tested by a number of research workers include rich and lean primary zones, premixing air and fuel, exhaust gas recirculation, variable area geometry, air assisted fuel injections and staged combustion.

(b)

To modify the fuel to reduce the  $\text{NO}_x$  emissions.

(c)

To use catalytic combustion to avoid high combustion temperatures and thus limit the quantities of  $\text{NO}_x$  produced (16).

(d)

The last technique which is inherently very attractive would not change current engine operating practices but would treat either the exhaust gas or the primary zone gas to

reduce  $\text{NO}_x$ . There are a number of techniques in the literature designed to reduce  $\text{NO}_x$  formation in the combustion system. The water/steam injection technique has been more fully developed than the other methods and has proven effective in reducing  $\text{NO}_x$  by better than 80 per cent (16).

#### 2.2.4 STEAM ADDITION

The injection of steam/water into combustion systems has been known for some time as a means of controlling  $\text{NO}_x$  emissions and increasing power output in the case of gas turbines (39, 40, 43, 53). Steam has the advantage in that the latent heat of vapourization does not have to be supplied by the turbine combustion. Steam increases cycle efficiency by 2 per cent for each per cent increase in the air (16). The advantages of steam injection were listed as:

- (1) Increase in turbine power.
- (2) Increase in thermal efficiency
- (3) Reduction in  $\text{NO}_x$  emissions.

The findings from the published literature suggests that the effectiveness of steam or water injection in reducing  $\text{NO}_x$  emissions is due to its higher heat capacity, thus reducing the flame temperature. The formation of  $\text{NO}_x$  in combustion systems is so highly temperature dependent (60) that a relatively small reduction in temperature can have a major effect in reducing  $\text{NO}_x$ .



The results of steam injection in gas turbine combustion chambers carried out by a number of workers in order to reduce  $\text{NO}_x$  emissions are summarised below.

Kalpatch and Koblisch (15) have determined the effectiveness of the injection of inert materials (water, steam) on the formation of oxides of nitrogen. Here water as liquid or steam is considered as an inert high heat (as well as latent heat) substance to be injected into the primary zone. Tests were conducted with water injection at various water-to-fuel ratios at several power levels while monitoring engine performance and exhaust emissions. The effect of steam on  $\text{NO}_x$  reduction was considered extremely encouraging since the results compare favourably with the calculated levels of reduction for the flow range investigated, thereby indicating that near optimum mixing had been achieved. Observation of the flame in the burner rig with steam injection revealed that its appearance changed from white luminescent to a semi-bluish haze, thereby indicating that a physical change was occurring with steam injection. Internal gas probing revealed some increase in local unburnt hydrocarbon level with steam injection; however, measurements at the burner exit indicated no net increase in total hydrocarbons. It was noted that no deterioration in burner exit temperature pattern occurred with steam injection, indicating that engine tests with steam could be carried out.

Kalpatch and Koblisch summarised from their experiments that  $\text{NO}_x$  can be substantially reduced by steam injection without significantly affecting engine operation and hardware durability. Their rig tests indicated that in order to realize the full potential from the injection of inert, high specific heat substances for  $\text{NO}_x$  retardation when running on liquid fuel, it will be necessary to attain the optimum distribution of the substance into the NO formation zone of the combustor. They finally concluded, however, that the feasibility of injecting water and steam directly into the gas turbine combustion chamber in order to retard NO formation was clearly demonstrated by engine and rig experiments as a practical means to control  $\text{NO}_x$  emissions.

Miyauchi Mori and Yamaguchi (42) worked on the effect of steam addition on NO formation. To achieve this purpose NO concentration profiles in methane/air premixed flames were measured under the condition of constant maximum flame temperature, with various concentrations of added steam. In order to do this experimentally the flow rates of methane and air were measured by rotameters and the reactants were electrically heated and introduced into the burner. Steam was generated by evaporating water in a glass container placed in a thermostatically controlled container and introduced into the burner through electrically heated piping. At this time a small amount of  $\text{N}_2$  gas was injected into the water to promote vaporisation of water. Methane air and steam were mixed uniformly and a premixed flame was produced. A quartz

probe was used to sample gases from the flame. From their experiments the following conclusions were made.

(a)

In the above study the physical effect of temperature decrease was eliminated. It was shown that NO concentration was reduced by steam addition even though the maximum flame temperature was kept constant. It was also shown that the amount of NO reduction by steam addition increases with  $\phi$  when the equivalence ratio was above stoichiometric and the reduced amount appeared noticeable when the added steam concentration exceeded 10 mol per cent.

It has been mentioned by Melton, Lestz, Quillian and Rambie (30) that there is a probability that oxides of sulphur ( $\text{SO}_x$ ) might also be removed from engine exhaust during operation with water injection. If so, this could make fuels with relatively high sulphur content look attractive, at least perhaps for stationary applications. It has been mentioned by researchers that the formation of  $\text{NO}_x$  and  $\text{SO}_x$  depends mainly on the temperature, atomic oxygen concentration and residence time (15, 40). So a process which reduces  $\text{NO}_x$  in combustion systems could be expected to reduce  $\text{SO}_x$  too. The addition of steam or water in the combustion system has proved an effective method of reducing  $\text{NO}_x$ , hence this system could also be adopted to reduce  $\text{SO}_3$ . Work can be done to inject steam or water into the combustion chamber in order to find the effect of it in the flame as this is where it is thought that most of the oxidation of  $\text{SO}_2$  takes place.

In view of the above it seemed logical that a research programme should be undertaken to investigate the effect of steam addition on  $\text{SO}_2$  oxidation. To enable this objective to be carried out a test rig was built based on a similar rig used by Ahmed and Zaczek (9). The rig consists of a combustion system which produces a premixed laminar flame, from the combustion of sulphur doped kerosene. The combustion took place in a combustion chamber made of refractory material and the gases passed through a quartz tube to avoid catalytic oxidation of  $\text{SO}_2$ . Steam was produced in a small marcet boiler and passed through heated copper piping into the combustion chamber. A chemical wet method described by Goksoyer and Ross (33) was used in this connection to determine the amount of  $\text{SO}_3$  in the sampled gases. The above investigation was carried out under controlled conditions.

### CHAPTER 3

#### 3.1 OBJECTIVE, EQUIPMENT AND MEASURING TECHNIQUE

##### 3.1.1 OBJECTIVE OF INVESTIGATION

The main objective of the research programme was to investigate the effect of steam injection on the oxidation of sulphur dioxide. To enable this work to be carried out a laboratory type rig was constructed based on the design of a combustor described by Ahmed and Zaczek (9).

A liquid fuel firing combustor with a laminar premixed flame was used in the investigation. The combustor had a quartz tube with five sampling parts placed along the length of the tube for gas sampling. A kinetic study was done to investigate the factors effecting  $\text{SO}_2$  oxidation. Finally, steam was produced in a Marcet boiler and injected in the combustion chamber. Gases were sampled and check for the  $\text{SO}_3$  concentration.

### 3.1.2 EXPERIMENTAL PROGRAMME

Increase the sulphur content of fuel (kerosene to 3.4% by weight) and investigate the following:

- (a) Investigate the stabilisation time of the apparatus by measuring exhaust gas temperature along the tube at regular intervals.
- (b) Investigate the temperature profile across the tube at various positions.
- (c) Investigate the amount of  $\text{SO}_3$  in the flue gases by varying the amount of excess oxygen.
- (d) Investigate the effect of residence time on  $\text{SO}_3$  in flue gases.
- (e) Investigate the effect of isothermal conditions on  $\text{SO}_3$  concentration in flue gases.
- (f) Investigate the effect of steam injection on  $\text{SO}_3$  by injecting steam at various positions of the flame, and to determine the best effective point of injection.

## EQUIPMENT

### 3.2.1 THE EXPERIMENTAL SYSTEM

A line diagram and the general layout of the experimental apparatus is shown in FIG 1 and Plate 1 respectively. The apparatus consists of three important parts.

- (i) The combustor
- (ii) Boiler and steam condenser arrangement
- (iii)  $\text{SO}_3$  sampling train.

### 3.2.2 THE COMBUSTOR

The combustor consists of four parts.

- (a) The fuel tank
- (b) The evaporating chamber
- (c) The combustion chamber
- (d) The combustion tube.

(a)

The fuel tank is a rectangular steel type of three litre capacity (Plate 2) which is fitted with a pressure gauge to show the actual pressure in the tank when pressurised by nitrogen gas. There is a nitrogen inlet line and fuel outlet line with an inline filter fixed on this line before the fuel reaches the rotameter. The fuel tank also has a glass sight gauge to indicate the fuel level. A Pressure relief valve was incorporated for safety purposes.

(b)

The evaporating chamber consists of a stainless steel cylinder 65 mm internal diameter and 85 mm length with a stainless steel sintered disc of 65 mm diameter and mesh size 250 fixed with the aid of a circlip at the front end of the cylinder. At the backend, the fuel and air inlets are mounted to a nozzle in such a way that the fuel air mixture atomises and leaves the nozzle into the evaporating chamber in a cone shape when cold, and probably in a cloud form when hot. The evaporating chamber is wrapped with a heating coil of 0.45 KW power capacity. The temperature inside the chamber was maintained around 120°C by the help of an "Electrothermal" thermostat. Due to the temperature of the evaporating chamber the air and fuel mixture entering the chamber evaporates and is forced through the sintered disc into the combustion chamber. A Cr/AL thermocouple of stem size 1.5 mm is mounted into the evaporating chamber to monitor the temperature inside the chamber. On initial starting it took about 15 minutes to warm up the chamber to 120°C.

(c)

The combustion chamber is made of fireclay enclosed in a mildsteel cylindrical casing. This chamber has 10 mm diameter holes drilled through to the centre of the chamber. When mounted on the frame together with the evaporating chamber these holes were at distances of 7.5, 17.5, 27.5, 67.5 and 147.5 mm from the sintered disc. The holes are fitted with steel tubes welded to the casing of the chamber so that the



centre line of the tubes and the holes are inline. These tubes could be coupled to the steam pipe whenever needed.

(d)

The combustion tube is of 76 mm internal diameter, and made out of quartz material in order to minimize catalytic action. Five holes of 10 mm diameter are drilled at a distance of 77, 327, 627, 927, 1227 mm away from combustion chamber end of the tube for gas sampling. Five Cr/AL thermocouples of stem size 1.5 mm are fixed vertically from the top of the pipe to measure the temperature at the sampling points.

The evaporating chamber, combustion chamber and combustion tube are mounted on a frame in such a way that the centre line of these are the same as appears in FIG 2. The first sampling port was 280 mm from the sintered disc (FIG 3) from where all the distance were measured. The other four sampling ports were located 300 mm apart from each other.

### 3.2.3 THE BOILER AND STEAM CONDENSER

Steam was produced in a small Marcet boiler of 2.0 litre water capacity. A working pressure of 5.2 bar (80 psig) was maintained during experiments. The boiler was heated by three bunsen burners and it took about 30 minutes to reach a steady pressure of 5.2 bar. A lever-weight operated safety valve, fitted to the boiler also acted as a means of pressure control (FIG 4). The boiler had a simple modification to incorporate a two way valve on its outlet line after the control valve. One pipeline from the two-way valve reached a condenser where the steam flow rate was measured.

The other pipeline from the two-way valve was connected to the combustion chamber (FIG 1). Both pipe connections were made of copper, equal in length and diameter. The steam pipe was wrapped with an Electrothermal heating coil rated at 0.45 kw and the temperature of the pipe surfaces maintained at  $190^{\circ}\text{C}$  by means of a thermocontrol switch. Five steam injection points were arranged in the combustion chamber and so five different inter-changing pipe arrangements were available.

#### 3.2.4 SAMPLING TRAIN

The sampling train was arranged as mentioned by Goksoyer and Ross (33). This consisted of a condenser, absorbants dryer and suction pump all connected in series. The condenser was a tubular spiral surrounded by a water jacket of pyrex glass (FIG 6). At the end of the spiral a grade 4 sintered glass disc was fitted which trapped any acid particles in the gas stream. A short quartz sampling probe was connected to one end of the condenser and inserted into the sampling port to sample gases from the combustion tube. A number of sampling probes with various dimensions are shown in FIG 7. A short probe with a  $90^{\circ}$  bend (FIG 7b) was chosen to be used as this was the best probe for sampling  $\text{SO}_3$ . Since the probe was short the gases passing through the probe were above  $150^{\circ}\text{C}$  and hence condensation in the probe was not possible. It was also possible to sample gases parallel to the flow due to the  $90^{\circ}$  bend.  $\text{SO}_2$  from the sampled gases was absorbed by passing the gas through hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) solution. This prevented acid damage to other instruments such as the

suction pump and gas meter which was used in the sampling train. A liquid trap and silica gel drying tower was used to keep the gas dry when passing through the gas meter. The gas samples were drawn through the condenser,  $\text{SO}_2$  absorber, liquid trap, drying tower and finally the gas meter by using a rotary vacuum pump. A diagrammatic view of the sampling train is shown in FIG 5. A second vacuum pump was used in conjunction with another drying tower for washing  $\text{H}_2\text{SO}_4$  from the condenser (plate 3).

### 3.2.5 PREPARATION OF FUEL

Some earlier workers (9, 28) have used kerosene with 3.4% sulphur in experiments probably due to the fact that typical boiler residual fuel contains about the same amount of sulphur. Hence, it was decided to raise the sulphur content of the fuel to 3.4% in this work. Domestic kerosene was tested for sulphur oxides in the rig and showed to have hardly any. By mixing approximate amount of carbon disulphide ( $\text{CS}_2$ ) to kerosene the sulphur content of the fuel mixture was raised to 3.4% (by weight). Calculations given in Appendix I show that a mixing ratio of  $\text{CS}_2$  to kerosene of 1:39 is required.

### 3.2.6 FUEL SUPPLY

The fuel was supplied from a tank as described before. The fuel was fed into the evaporating chamber from a stainless steel tank pressurized by  $\text{O}_2$  free  $\text{N}_2$  gas and metered through a calibrated rotameter. The rotameter was manufactured by Fisher Control Limited and designed for the specific use of kerosene and calibrated in  $\text{CM}^3\text{min}^{-1}$  at  $20^\circ\text{C}$ . A maximum

temperature variation of about  $3^{\circ}$  was observed in the laboratory. As the volume flow rate was proportional to  $\frac{1}{\sqrt{p}}$ , this variation in temperature gave negligible changes in the volume flow rate of fuel and is hence ignored in calculations.

### 3.2.7 AIR SUPPLY

Combustion air was obtained from the Polytechnic's central compressed air supply. It entered the system through a filter and rotameter for metering. The rotameter was a Fisher Control type 2000 series designed for the specific use of air and calibrated in litres  $\text{min}^{-1}$  at  $15^{\circ}\text{C}$  and 5 psig. A maximum temperature variation of about  $3^{\circ}\text{C}$  was observed in the laboratory. This variation in temperature gave a negligible change in volume flow rate of the air and is hence ignored in calculations. A general arrangement of the metering instruments described above are shown in plate 2.

### 3.2.8 AIR FUEL RATIO

The excess  $\text{O}_2$  in the flue gas was kept constant, throughout the tests at 4.5% (by volume), by keeping the air to fuel ratio constant. The calculation of air to fuel ratio to have 4.5%  $\text{O}_2$  is given in appendix V. This excess  $\text{O}_2$  was checked and corrected using a Servomex Oxygen analyser (type OA.101) during the tests. This procedure was carried out every time before samples were taken from the flue gases. During sampling it was important to have a uniform flow of gases across the tube. By maintaining the air and fuel flow rates fixed it was expected that a uniform flow of gases will

be in the tube. The Reynold number was calculated and the flow pattern was determined to be laminar. Calculation of Reynold number is given in Appendix IV.

### 3.2.9 STARTING PROCEDURE

It was ensured that all valves were shut. The after burner was started at the beginning of each test run to burn any unburnt gases escaping to the duct. This procedure eliminated the possibility of any explosions in the duct and also helped in reducing the amount of pollution released to the atmosphere.

The evaporating chamber heaters were energized and the chamber temperature was raised. When the temperature reached  $120^{\circ}\text{C}$  the burner was ready for starting. The valve on the air rotameter was opened for atomisation and combustion air to enter the evaporating chamber. The fuel tank was pressurised with oxygen free nitrogen and the tank pressure was set at about 0.7 bar (10 psig). The valve on the fuel rotameter was opened and the fuel  $F^0$  rate was set at  $6 \text{ cm}^3 \text{ min}^{-1}$ .

When a white cloud appeared from the combustion chamber the burner was ignited using a bunsen flame. A short while after combustion had started, the air and fuel flow rates were very slowly adjusted to the required condition in order to obtain 4.5% excess oxygen in the combustion gases. If the combustion failed unburnt fuel vapour was seen through the chamber and immediately the fuel valve was shut and the combustion chamber purged with air. Once the combustion started properly it was left running for about an hour and a half to reach a steady

state before any samples were taken. At the completion of a test, fuel flow was stopped and the evaporating chamber heater deenergized. The air flow was left on for about ten minutes to cool the apparatus and then all valves were closed.

## MEASUREMENT TECHNIQUE

### 3.3.1 TEMPERATURE MEASUREMENT

The temperature of the gas was measured with a 40  $\mu$ m diameter Platinum/Platinum 13% rhodium bare wire thermocouple with a bead size diameter between 70 and 80  $\mu$ m (FIG 8). This was used in conjunction with an "Apple IIe" microprocessor system. The thermocouple signal was fed to a differential amplifier with an amplification factor of 100. It was then simultaneously displayed on an oscilloscope and digitised by an analogue to digital converter. The signal was then processed by the "Apple IIe" microprocessor system and the temperature displayed on the monitor. At the end of the run a table of temperature against radial distance traverse was printed. A precision crank arrangement was engaged to locate the position of the thermocouple at the required distances in the tube (plate 4). As the temperature measured by the thermocouple was subjected to errors a radiation correction was made to the temperature measurements obtained (37). A sample radiation correction calculation is given in appendix IX.

A second 1.5 mm probe stem diameter Cr/Al thermocouple, in conjunction with a Comark electronic thermometer was used at similar positions to the fine wire thermocouple. Hence, it was possible to relate both temperatures graphically (FIG 18). Therefore, by using the simple second arrangement it was possible to measure the gas temperature and find the actual temperature of the gas from FIG 18.

### 3.3.2 OXYGEN MEASUREMENT

The excess oxygen in the flue gases was measured by using a "Servomex" portable oxygen analyser type OA 101 MK11. The principle of operation of this equipment is explained in appendix 11. Plate 5 shows the analyser in use to check the oxygen percentage of the flue gas at Port 2.

### 3.3.3 CARBON DIOXIDE MEASUREMENT

The carbon dioxide concentration in the flue gases was measured by FYRITE CO<sub>2</sub> Indicator. This is fully described in Appendix X.

### 3.3.4 SULPHUR TRIOXIDE MEASUREMENT

The concentration of SO<sub>3</sub> was measured by the chemical wet method described by Goksoyer and Ross (33). The sampling train used in the experiment is shown in FIG 5. A short quartz sampling probe was connected to the condenser. The probe was positioned in such a way so as to draw samples from the centre of the tube and parallel to the gas flow. The probe is made of quartz and suitable for a flue gas temperature around 800°C. Since it was a short probe the

question of condensation in the probe was eliminated when the sampling gas temperature was above 300°C.

As the gas was drawn through the condenser, which was maintained between 60-90°C the sulphuric acid mist condensed on the walls of the condenser tube. The residual gases then passed through Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) solution where all the sulphur dioxide ( $\text{SO}_2$ ) was absorbed and then through an empty wash bottle to trap any water carried over from  $\text{H}_2\text{O}_2$  solution and through silica gel to remove all the moisture in the gas stream. Finally, the gas passed through a gas meter to the atmosphere. The volume flow rate of the gas sample was indicated by the gas meter. The sampling rates can be regulated by a needle valve which was incorporated in the sampling line.

When the required amount of gases were sampled the condenser was removed from the line and fixed on a washing train as shown in Plate 3. The condensate was washed out using 50 ml washing solution which consists of a mixture of 5% by volume of isopropanol with distilled water and bromophenol blue indicator.  $\text{SO}_3$  was determined by titration of the washed sample against 0.02N sodium hydroxide ( $\text{NaOH}$ ) and substituting values of the equation described by Goksoyer and Ross (33). Determination of  $\text{SO}_3$  by Goksoyer and Ross method is more fully described in Appendix VII.



## CHAPTER 4

### 4.1 RESULTS

The results of the experiments are plotted and presented in this chapter together with the necessary datas.

- Port1-187cm from disc
- △ Port2-487cm from disc
- + Port3-787cm from disc
- × Port4-1087cm from disc

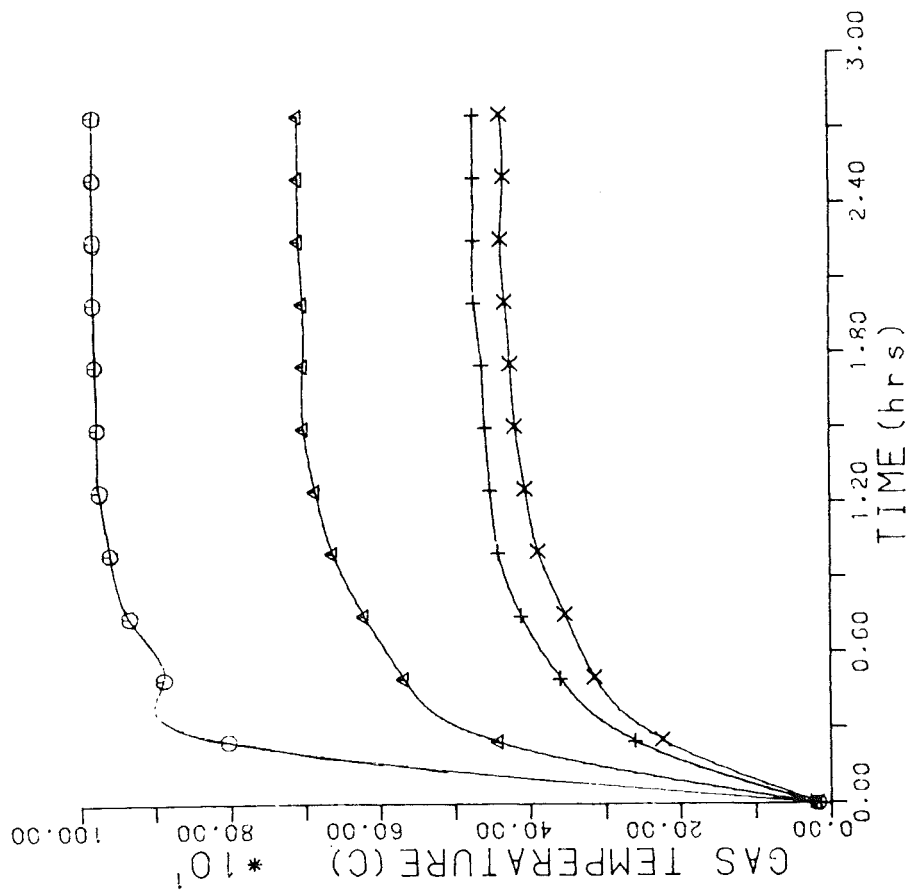


FIG. 9 Gas temperature with time.

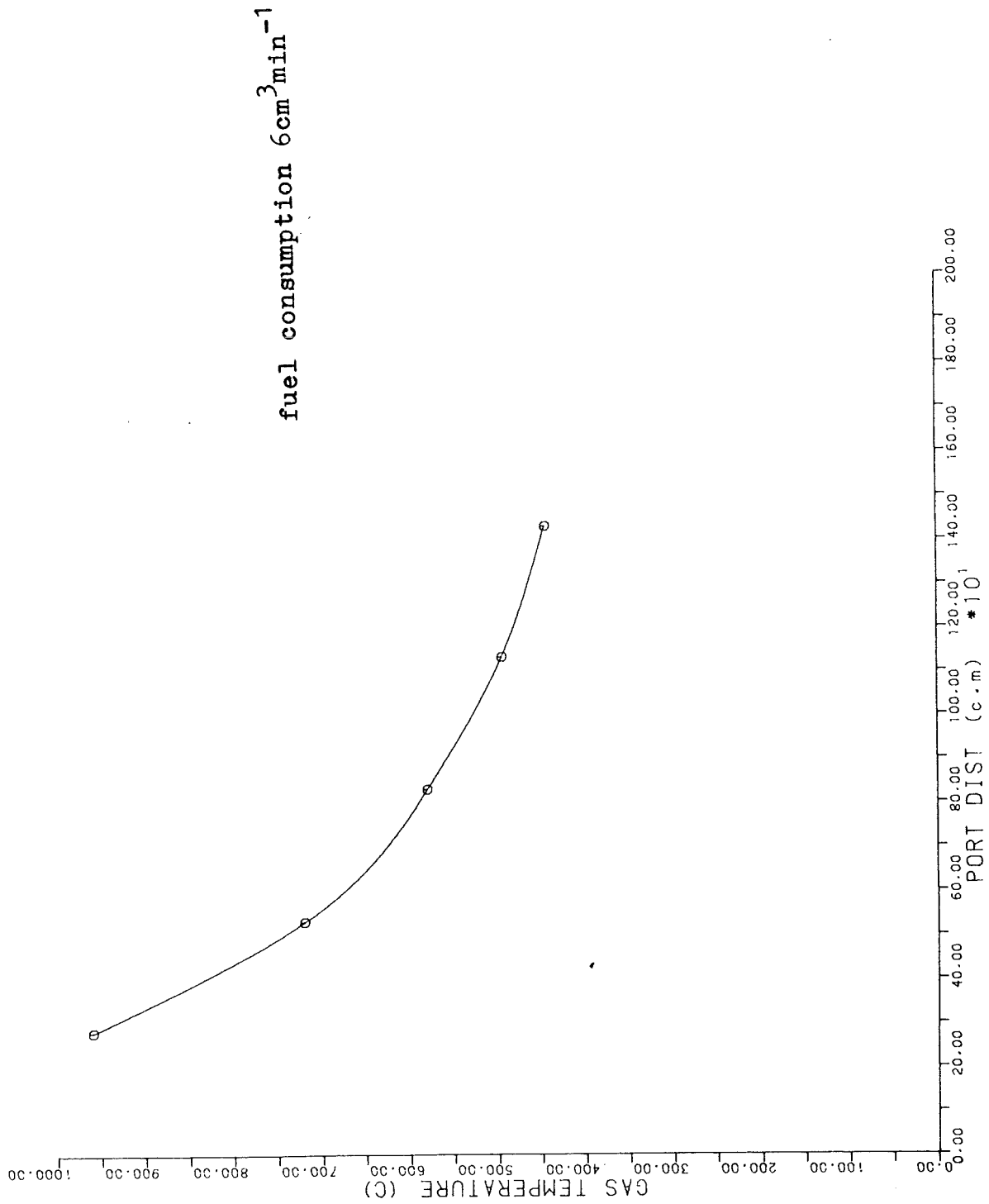


FIG.10 Typical temperature profile along the tube.

measurements taken in port 4

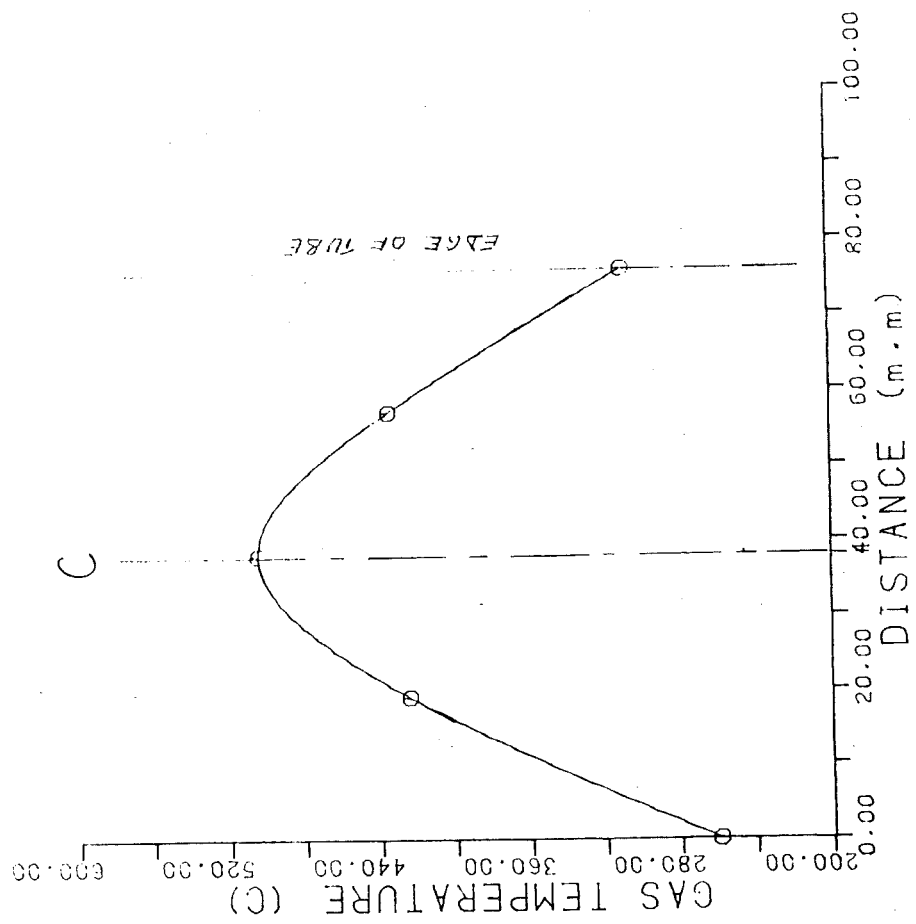


FIG. 11 Temperature profile across tube.

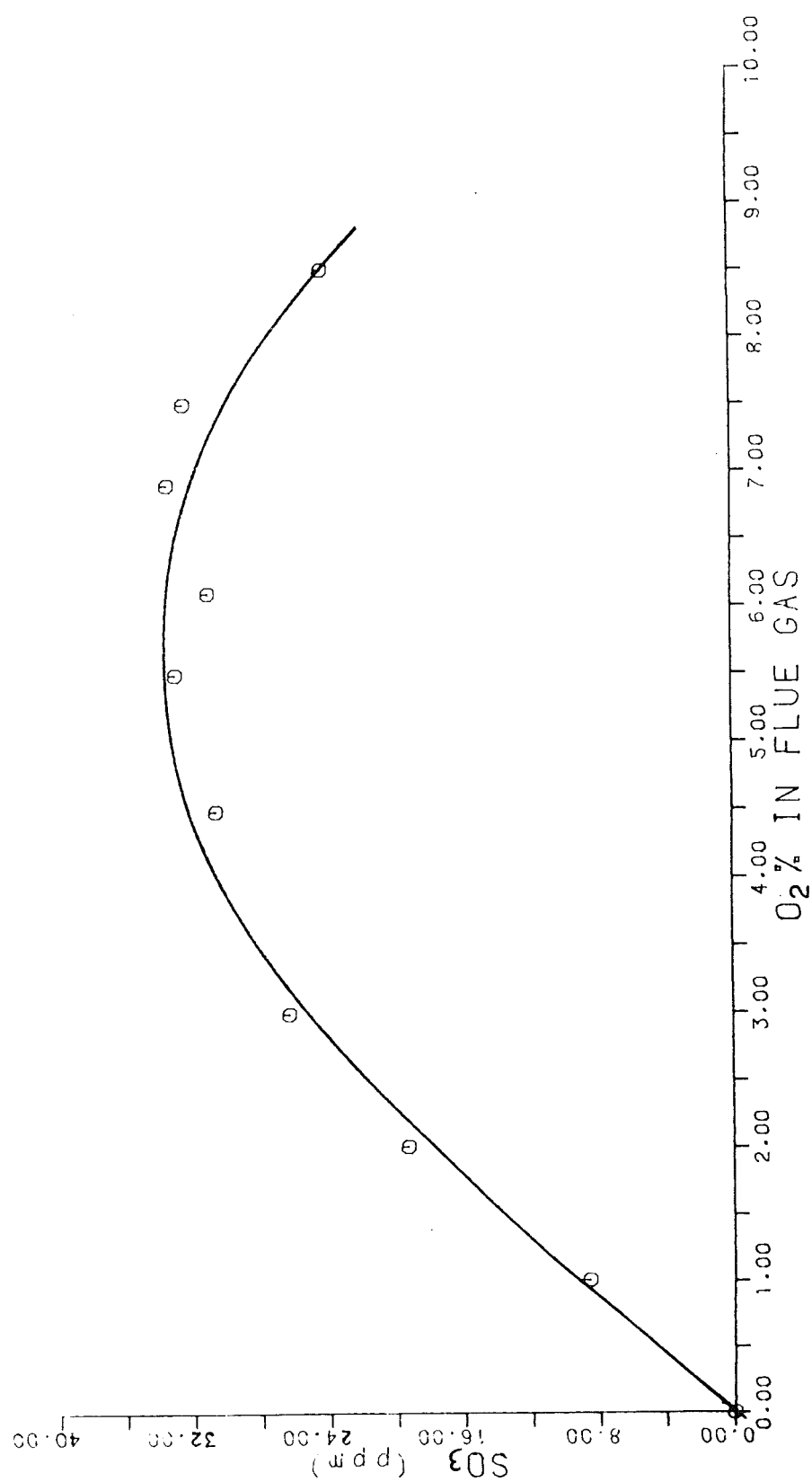


FIG.12 Concentration of  $\text{SO}_3$  with  $\text{O}_2\%$ .

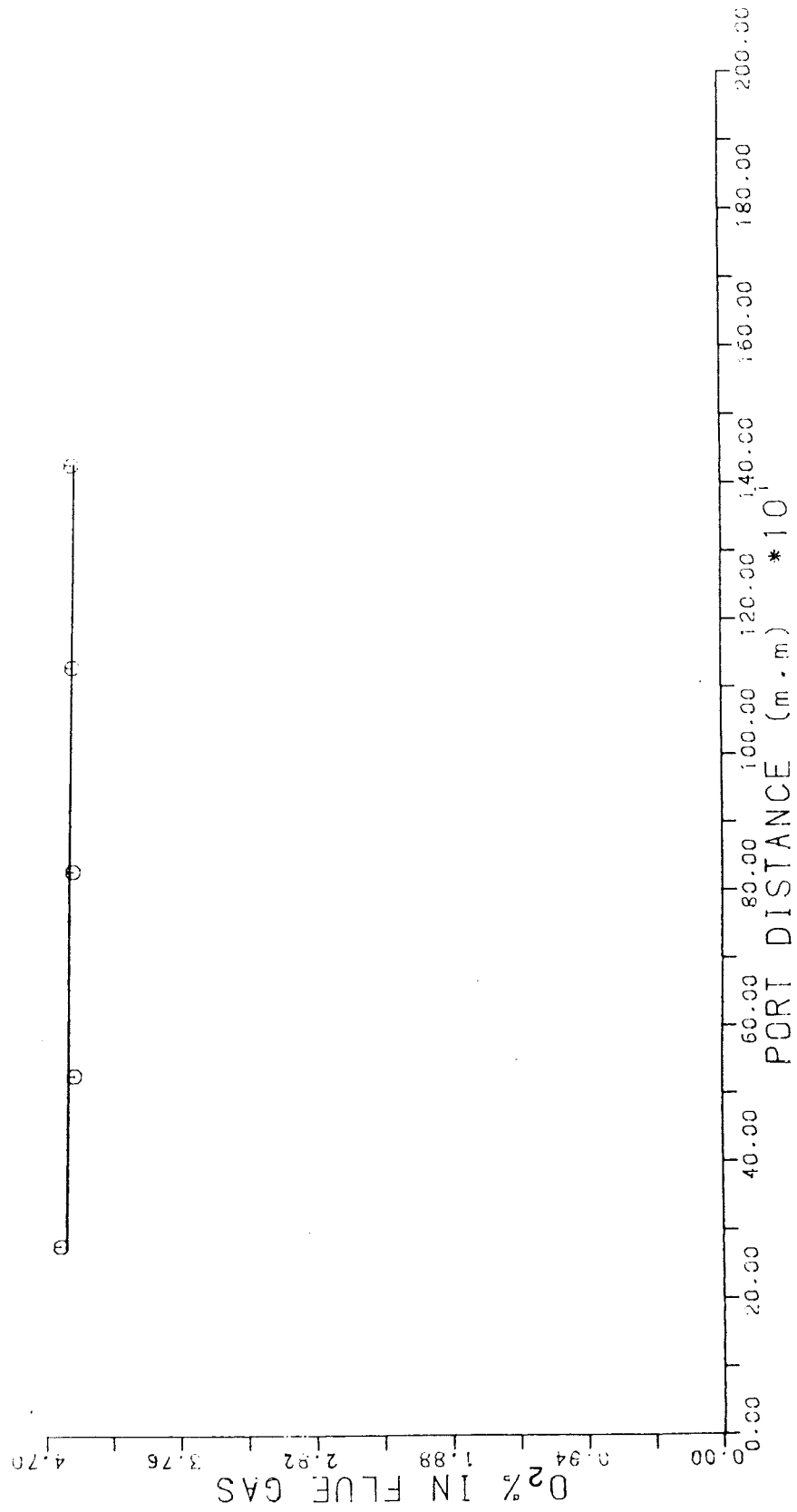


FIG. 13 Oxygen percentage with port distance.

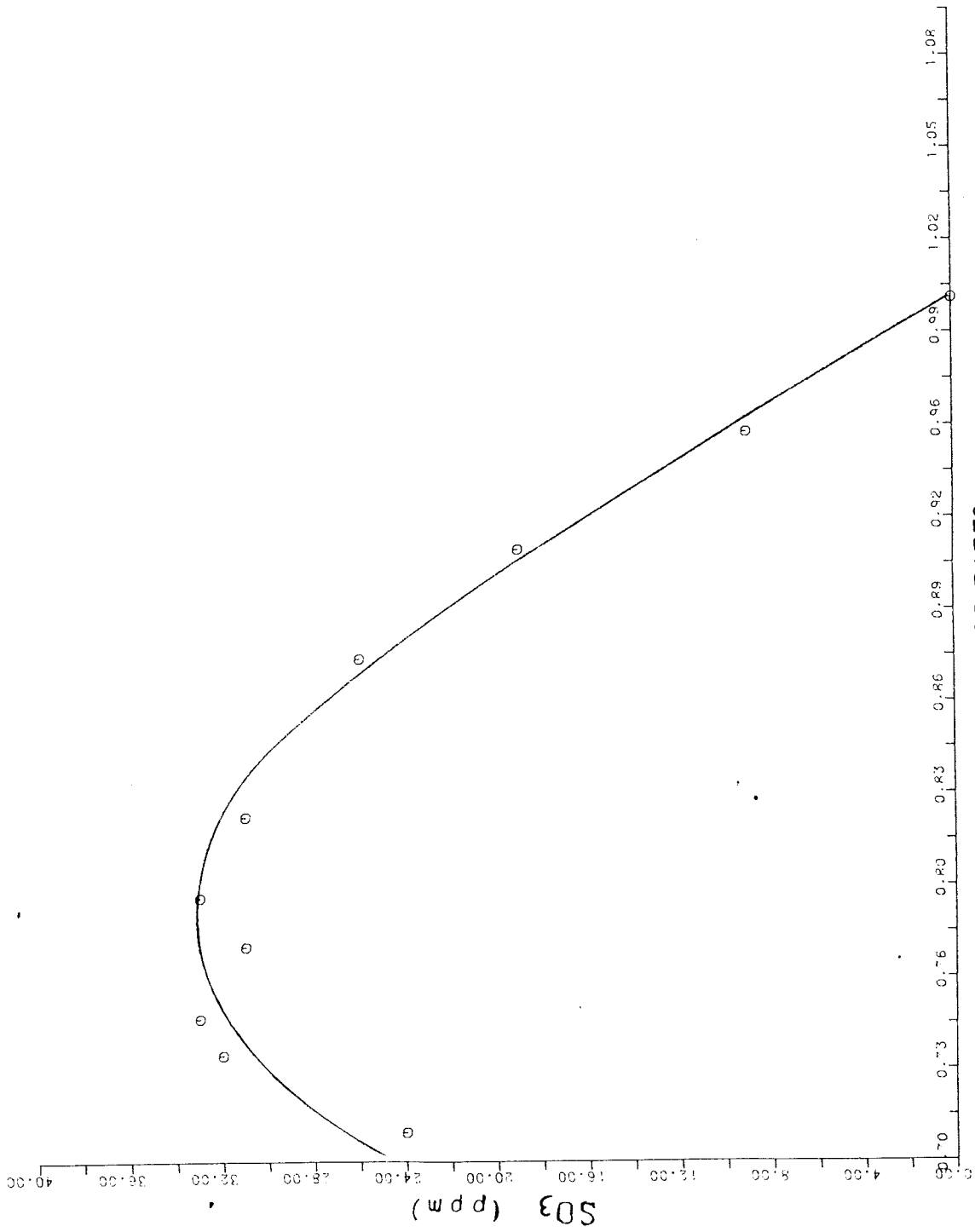


FIG. 14  $\text{SO}_3$  with equivalence ratio.

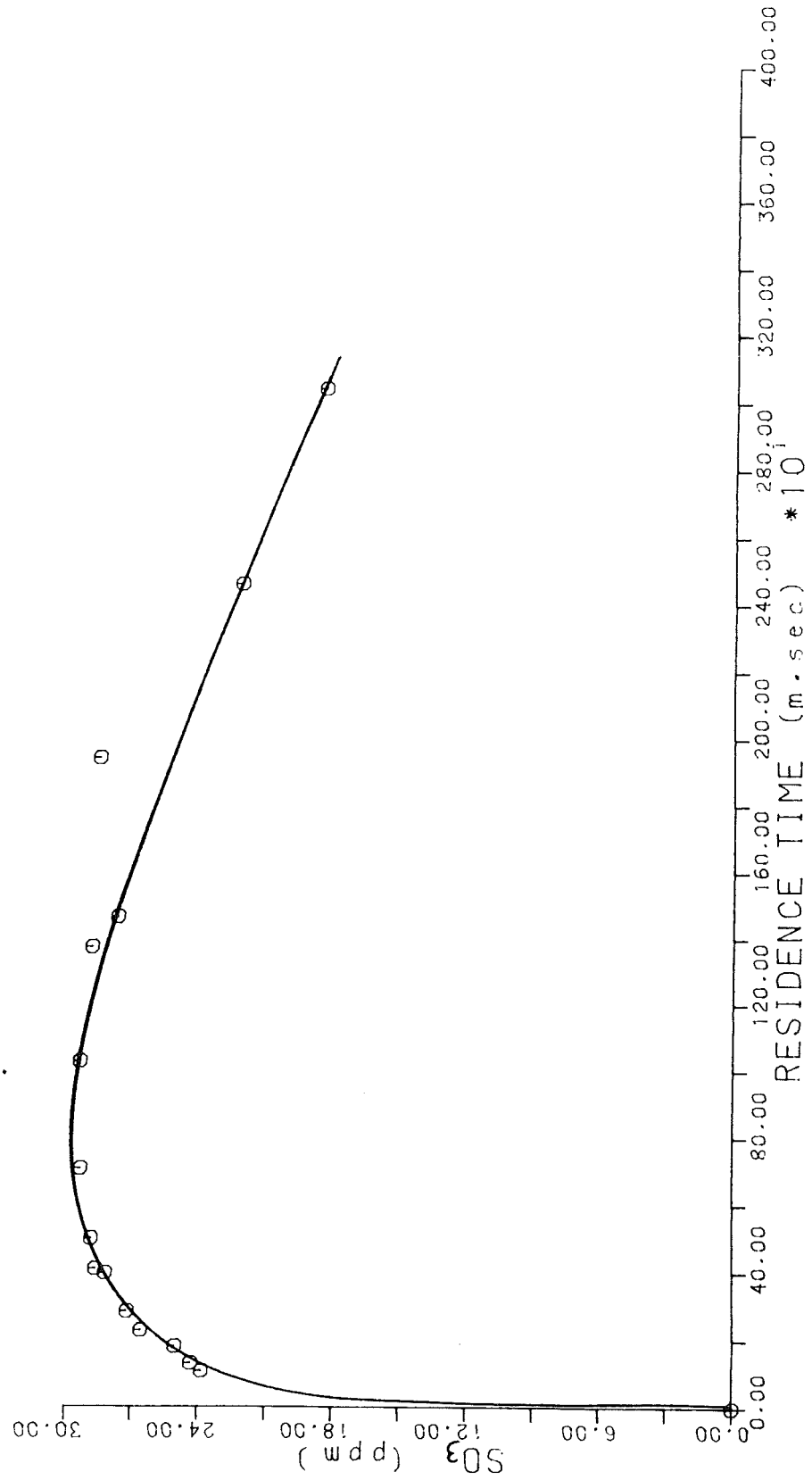


FIG. 15 Concentration of  $\text{SO}_3$  with residence time.



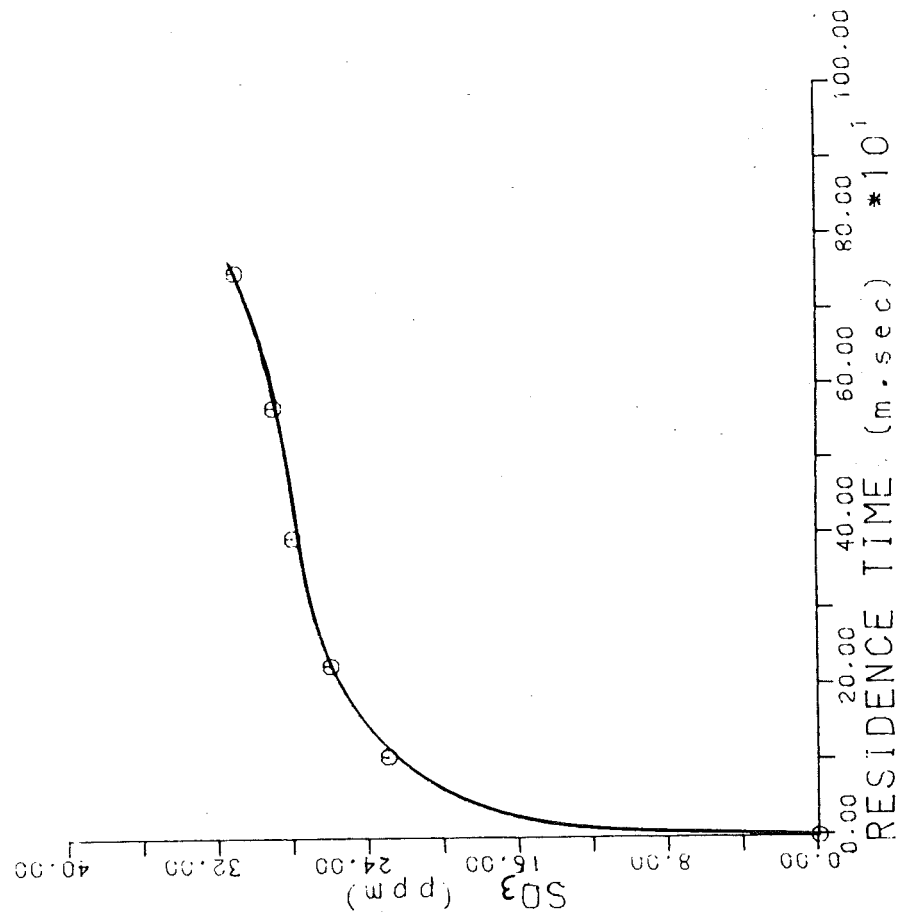


FIG. 16 Concentration of  $\text{SO}_3$  with residence time  
(near isothermal condition).

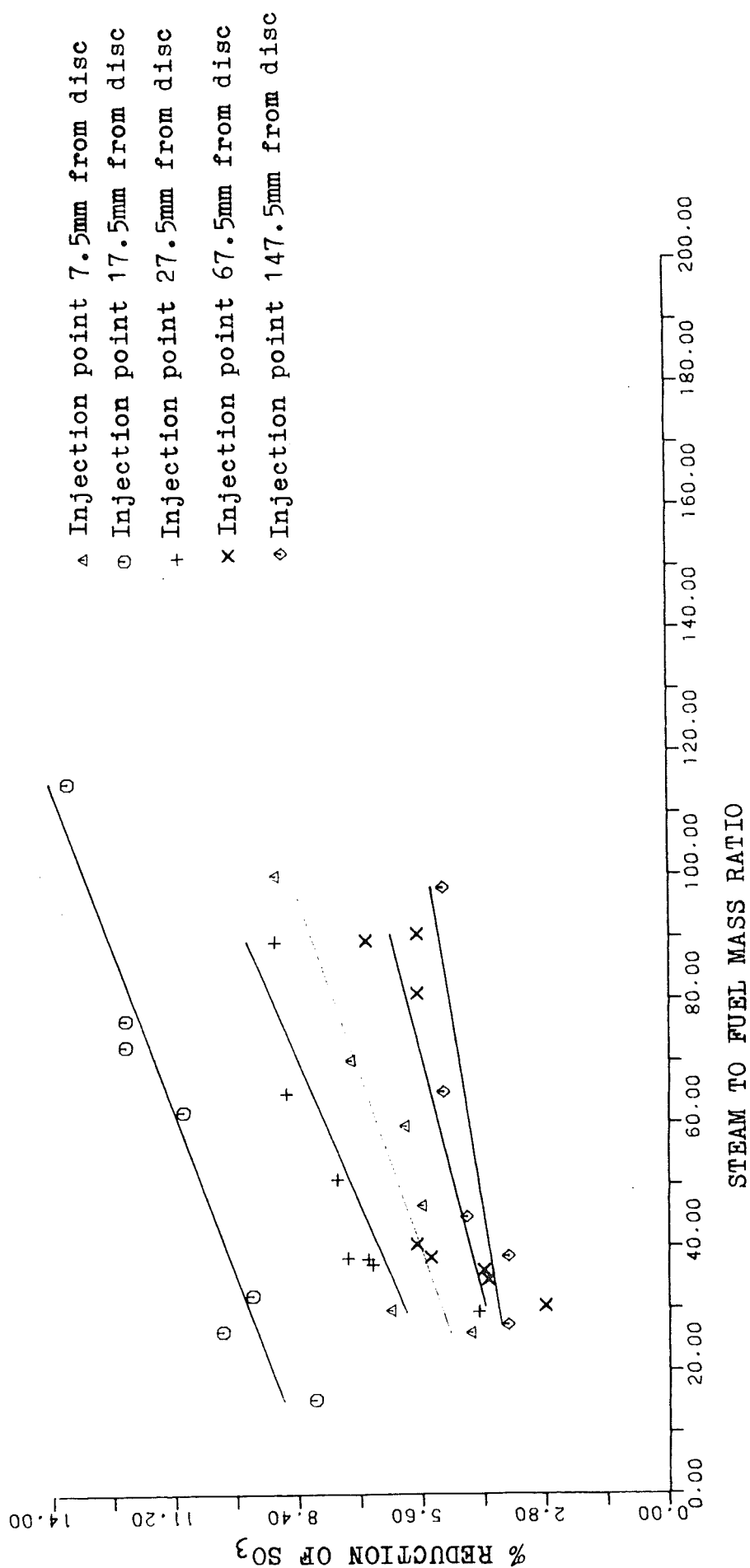


FIG. 17 % Reduction of  $\text{SO}_3$  with steam to fuel mass ratio.

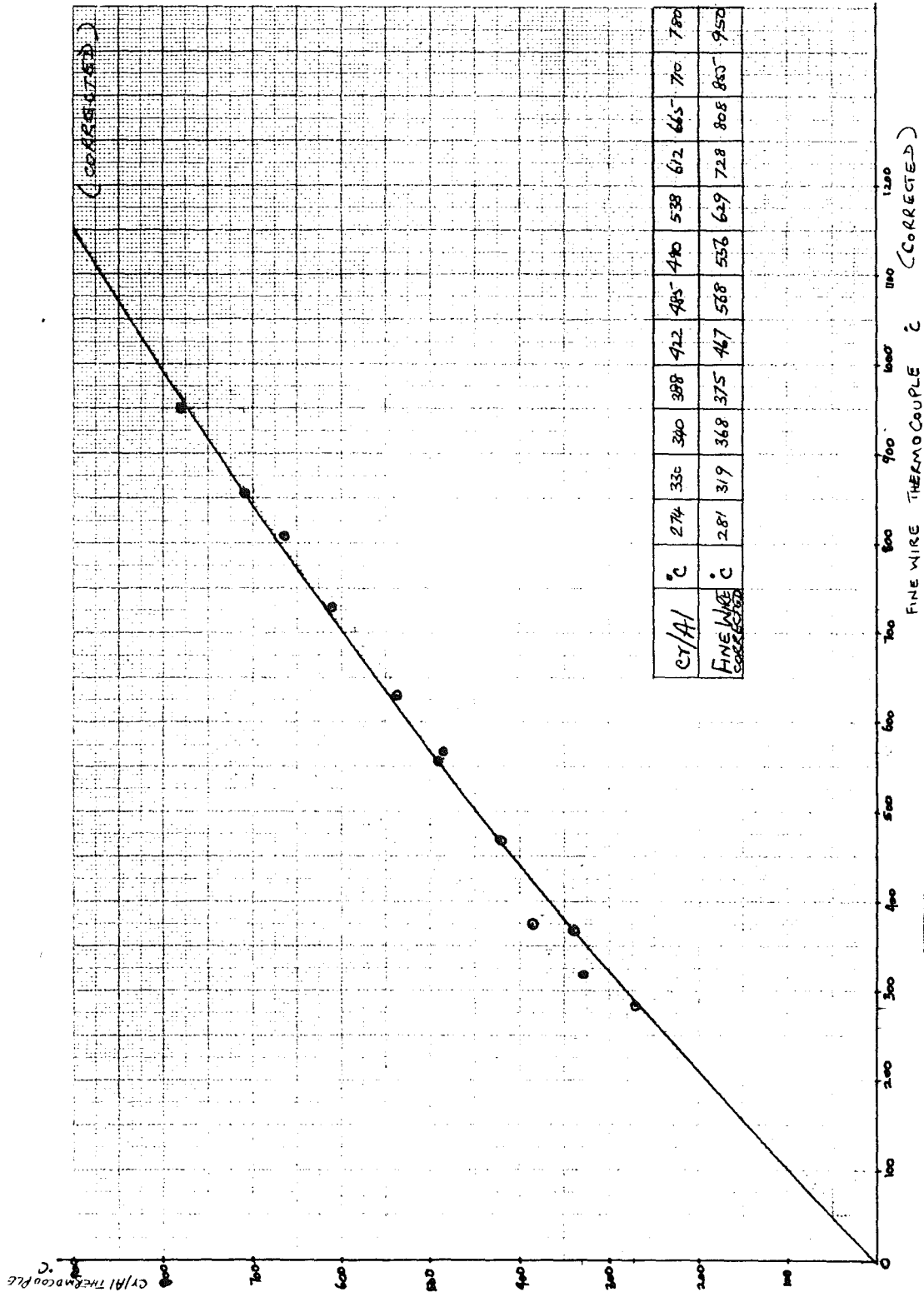


FIG. 18 Correlation of Cr/Al thermocouple measurement with corrected fine wire thermocouple measurement.

TIME (hours)	TEMP (°C) PORT 1	TEMP (°C) PORT 2	TEMP (°C) PORT 3	TEMP (°C) PORT 4
0	20	20	20	20
0.25	805	442	260	225
0.50	890	567	360	316
0.75	935	620	412	355
1.00	960	662	442	390
1.25	975	685	452	407
1.50	977	700	458	420
1.75	980	700	462	425
2.00	982	700	472	432
2.25	982	705	472	437
2.50	982	705	472	433
2.75	982	705	474	437

TABLE 4.1.1 DATA FOR FIG 9

PORT DISTANCE (cm)	GAS TEMP (°C)
280	960
530	720
830	580
1130	495
1430	445

TABLE 4.1.2 DATA FOR FIG 10.

DISTANCE FROM EDGE OF TUBE (MM)	GAS TEMP (°C)
0	260
19	425
38	505
57	435
76	310

TABLE 4.1.3 DATA FOR FIG 11

O <sub>2</sub> PERCENTAGE	SO <sub>3</sub> (ppm)
0	0
1.0	9
2.0	19
3.0	26
4.5	31
5.5	33
6.1	31
6.9	33
7.5	32
8.5	24

TABLE 4.1.4 DATA FOR FIG 12

PORT DISTANCE (cm)	O <sub>2</sub> PERCENTAGE
280	4.6
530	4.6
830	4.5
1130	4.5
1430	4.5

TABLE 4.1.5 DATA FOR FIG 13



EQUIVALENCE RATIO $\phi$	SO <sub>3</sub> (ppm)
1.0	0
0.95	9
0.91	19
0.87	26
0.82	31
0.79	33
0.77	31
0.75	33
0.73	32
0.71	24

TABLE 4.1.6 DATA FOR FIG 14

RESIDENCE TIME (m sec)	SO <sub>3</sub> (ppm)
0	2
107	23
130	24
180	25
227	26
284	27
397	28
410	28
500	29
710	29
1030	29
1370	28
1460	27
1935	28
2460	22
3040	18

TABLE 4.1.7 DATA FOR FIG 15

RESIDENCE TIME (m sec)	SO <sub>3</sub> (ppm)
0	0
107	23
227	26
397	28
570	29
750	31

TABLE 4.1.8 DATA FOR FIG 16

STEAM TO FUEL MASS RATIO %	% REDUCTION OF SO <sub>3</sub>
15.1	8
26.2	10.1
32	9.4
61.7	11.0
72.4	12.3
76.6	12.3
114.9	13.6

TABLE 4.2.0 DATA FOR FIG 17  
(INJECTION POINT 17.5 MM)

STEAM TO FUEL MASS RATIO %	% REDUCTION OF SO <sub>3</sub>
30.4	2.8
34.7	4.1
36.2	4.2
38.3	5.4
40.4	5.7
80.9	5.7
89.4	6.8
90.5	5.7

TABLE 4.2.1 DATA FOR FIG 17  
(INJECTION POINT 67.5 MM)

STEAM TO FUEL MASS RATIO %	% REDUCTION OF SO <sub>3</sub>
26.2	4.5
29.8	6.3
46.7	5.6
59.6	5.9
70.2	7.2
100	8.9

TABLE 4.2.2 DATA FOR FIG 17  
(INJECTION POINT 7.5 MM)

STEAM TO FUEL MASS RATIO %	% REDUCTION OF SO <sub>3</sub>
29.6	4.3
37.2	6.7
38.1	6.8
38.3	7.2
51.0	7.5
64.9	8.6
89.4	8.9

TABLE 4.2.3 DATA FOR FIG 17  
(INJECTION POINT 27.5 MM)

STEAM TO FUEL MASS RATIO %	% REDUCTION OF SO <sub>3</sub>
27.2	3.6
38.3	3.6
44.7	4.6
64.9	5.12
97.9	5.12

TABLE 4.2.4 DATA FOR FIG 17  
(INJECTION POINT 147.5 MM)

## CHAPTER 5

### 5.1.0 DISCUSSION

It can be seen that the combustor needed about 1.5 hours (FIG 9) to stabilize, ie, the temperature in each port reached a steady state provided all other parameters were maintained constant. It is after this stage that the gases sampled at these ports will have steady values. It can be seen that ports 1, 2, 3 and 4 reached about 975, 700, 460, 420°C respectively. The ports were 187, 487, 787, and 1087 mm respectively from the disc of the combustor. The above results were obtained from a silica tube combustor of 74 mm id and 82 mm od which was discarded later due to material failure at the combustor end.

It must be pointed out that  $\text{SO}_3$  is a highly reactive gas and minute in quantity, so great care was taken to make sure that the sampling of the gas was done properly. Much time was spent in perfecting the sampling technique using the chemical wet methods described in Appendix VII. A number of factors effect the final value of  $\text{SO}_3$  during experimentation. The excess oxygen, the gas temperature, and the fuel sulphur content have a greater effect on the  $\text{SO}_3$  concentration. A list of the factors effecting the concentration are given in Appendix VIII.

In the combustion process, temperature plays an important part in the formation of  $\text{SO}_3$ . So it is essential that the gas temperature is maintained steady during sampling of the gases. FIG 10 shows a typical temperature profile along the

quartz tube combustor of 76 mm id 80 mm od and at port distance 280, 530, 830, 1130 and 1430 mm away from the disc (FIG 3) where the flame was supposed to originate. In FIG 11 a temperature profile across the tube is shown which was taken at port 4 of the combustor. It appears that the maximum temperature is at the centre of the tube. The parabolic shape of the temperature profile indicates that the flow in the tube is laminar. This is further reinforced by the calculations given in Appendix IV. The Reynold number was calculated using the mean velocity of the gases in the tube and a specimen calculation of the velocity is given in Appendix XI.

Oxygen in the flame gases is said to be one of the main oxidising agents of  $\text{SO}_2$  through either atomic oxygen or catalytic route. The former could happen only when the temperature of the gas is sufficiently high whereas the latter could take place at lower temperatures. So it is imperative to keep excess oxygen to a minimum in combustion process to minimise unwanted gas formation ie  $\text{SO}_3$ ,  $\text{NO}_x$  etc. Experiments carried out with various percentages of excess oxygen show that the maximum amount of  $\text{SO}_3$  formed was at about 5.5% (FIG 12). During the sampling, the air fuel ratio was maintained to keep the excess oxygen at 4.5%. Similar work (9) has been done with the same amount of excess oxygen. Hence the value of excess oxygen was chosen for comparative study. Analysis of  $\text{O}_2\%$  along the tube (FIG 13) shows that steady conditions were maintained. The  $\text{O}_2\%$  was



was checked with the use of a Servomex oxygen analyser (Type OA 250) which was calibrated every time before it was used.

It can be seen from FIG 14 that the  $\text{SO}_3$  in the flue gases reduced with the increase of equivalence ratio  $\phi$ . As the equivalence ratio reached one the  $\text{SO}_3$  content also became zero since there will not be any oxygen in excess during stoichiometric combustion. At higher values of  $\phi$  the combustion becomes fuel rich and flame becomes smokey. It is also evident from the figures that when the equivalence ratio decreases below 0.78, the concentration of  $\text{SO}_3$  also decreases. This could be due to the dilution effect of the gases by the excess air.

FIG 15 shows the effect of residence time on  $\text{SO}_3$  formation. It can be seen that the value of  $\text{SO}_3$  increased with the time initially and then decreased as it passed along the tube. This shows that,  $\text{SO}_2$  initially associated with oxygen to form  $\text{SO}_3$ . As the newly formed  $\text{SO}_3$  passed along the tube with increasing residence time, dissociation of  $\text{SO}_3$  to  $\text{SO}_2$  took place, hence the drop in  $\text{SO}_3$ . In this investigation a quartz combustion tube was used to minimise the catalytic effect of  $\text{SO}_2$  being oxidised. Hence, the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  can be attributed mainly to atomic oxygen which could have been generated from CO oxidation as described by Semenov (24) or Lewis and Von Elbe (25) or by thermal decomposition of oxygen. It can be said that combustion of kerosene involved carbon monoxide oxidation. Hence, the above speculations could be possible explanations for O atom formation. It can be seen

that the results agree well with the results obtained by Hedley and Ahmed. It was also found that the  $\text{SO}_3$  present in the gas was very much in excess of theoretical equilibrium concentrations, calculation shown in Appendix VI. A further extension of this work was done by creating a near isothermal condition in the tube and the results obtained under these conditions show that  $\text{SO}_3$  actually increased as the residence time increased (FIG 16). This phenomenon can be explained in terms of a longer residence time for the gases at high temperature due to the influence of external heaters. Compared with many transient species present in the initial stages of the flame, the concentrations of CO and  $\text{SO}_2$  are large. CO being more reactive than  $\text{SO}_2$  will readily react with (O) to form  $\text{CO}_2$  and oxidation of CO will be complete in the initial stages of the flame. A comparison of the rate of CO reaction with O and  $\text{SO}_2$  reaction with O is given in Appendix III with the major assumption that all carbon and sulphur in the fuel is converted to CO and  $\text{SO}_2$  respectively in the first instance. If, however, the gas temperature is raised along the post-flame zone the reaction zone is likely to be increased enabling more time for  $\text{SO}_2$  to react with atomic oxygen, ie, in this enhanced O atom zone  $\text{SO}_2$  will take precedence over CO in reacting with O atoms, as most of the CO molecules will have been converted to  $\text{CO}_2$  at this stage. Hence, the concentration of  $\text{SO}_3$  will appear to be more at higher temperatures along the combustion tube (9, 45).

Figure 17 shows the second part of the results where it can be seen that injection of steam in the combustion chamber gave

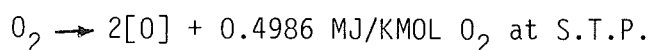
a reduction in the formation of  $\text{SO}_3$ . The reduction does not appear to be very significant compared to the amount of steam injected. This reduction varied with the point and rate of injection. It was thought that the flame was the best effective area where steam should be injected as the temperature near this zone will be high enough for H and OH radicals to attack atomic oxygen. A computer package was used to get the best possible line through the points of various tests carried out at various injection points in the combustion chamber. It can be seen that a reasonable reduction of  $\text{SO}_3$  was obtained when steam was injected at 17.5 mm from the disc where the flame was actually produced. Steam injection in other points did not give a better reduction of  $\text{SO}_3$ , though the reduction tended to increase as the steam to fuel mass ratio increased. At points 67.5 and 147.5 mm the steam injection process gave a small reduction of  $\text{SO}_3$ . It appears that at these points the variations in the percentage reduction of  $\text{SO}_3$  for different steam to fuel mass ratios were not appreciable. So it can be taken that when steam was injected into the right place of the flame, perhaps the reaction zone, considerable achievement on the suppression of  $\text{SO}_3$  can be obtained.

The flame in the combustion chamber can be divided into three important zones named as preheat zone, true reaction zone and post flame zone. Since steam injection in the 17.5 mm point gave a greater reduction in  $\text{SO}_3$  value it can be assumed

that this could have been in the reaction zone of the flame where the actual oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  probably took place with atomic oxygen.

Introduction of steam could firstly reduce the peak flame temperature and act as a mopping up agent of atomic oxygen thereby reducing  $\text{SO}_3$ .

Injection of steam in larger quantities viz, greater steam to fuel mass ratio could reduce the peak flame temperature by dilution effect which could lead to a decrease of  $\text{SO}_3$  formation. It can be seen from the following equation:

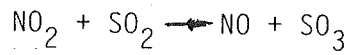


that O atom formation from its molecule needs high energies. Hence, a decrease in the peak flame temperature could reduce the formation of atomic oxygen.

Miyauchi, Mori and Yamaguchi (42) have produced a table of 51 elementary reactions from which reaction 21 and 20 are given below:



It can be seen from these reactions that O atoms are absorbed by  $\text{H}_2\text{O}$  and OH to create OH and  $\text{H}_2$  and  $\text{O}_2$  which thereby reduced the available atomic oxygen for further oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ . It is also given elsewhere (8, 26) that the  $\text{NO}_2$  formed in the combustor can catalyse  $\text{SO}_2$  homogeneously. The following equations are given to show the route of reaction of this process.



It has been well established that the injection of steam reduces  $\text{NO}_x$  in combustion systems. Hence, there is a possibility that the steam injected reduced NO formation in the combustor and thereby reduced oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ .

## CHAPTER 6

### 6.1.0 CONCLUSIONS

1. The level of  $\text{SO}_3$  content in flue gases reaches a maximum at about 5.5% excess oxygen concentration in combustion gases after which it starts to decline.
2. Decrease in equivalence ratio from one to 0.78 increases concentration of  $\text{SO}_3$ , below 0.78 the  $\text{SO}_3$  concentration tends to decrease.
3. The results obtained about  $\text{SO}_3$  concentrations with residence time shows similarities to the results obtained by Hedley and Ahmed. Hence, the support of the consecutive reaction theory
$$\text{SO}_2 + \text{O} \xrightarrow{K_1} \text{SO}_3 \xrightarrow{K_2} \text{SO}_2 + \frac{1}{2}\text{O}_2$$
is conclusive.
4. Consecutive reaction theory does not hold good under isothermal conditions, ie,  $\text{SO}_2$  with a longer residence time at high temperatures can react with atomic oxygen in that high intensity zone to form  $\text{SO}_3$ . Hence,  $\text{SO}_3$  concentration increased during isothermal conditions instead of decreasing due to dissociation.
5. Injection of steam in the combustion systems has an appreciable effect on the formation of  $\text{SO}_3$ .
6. The place of injection of steam, ie, the point of injection into the flame has a profound effect in the oxidation rate of  $\text{SO}_2$ .

7. Steam to fuel mass ratio has been shown to have an influence in the reduction of  $\text{SO}_3$  concentration. Our experiments show that 20% and 100% of steam to fuel mass ratio gave reductions in  $\text{SO}_3$  concentrations of 9% and 13% respectively.

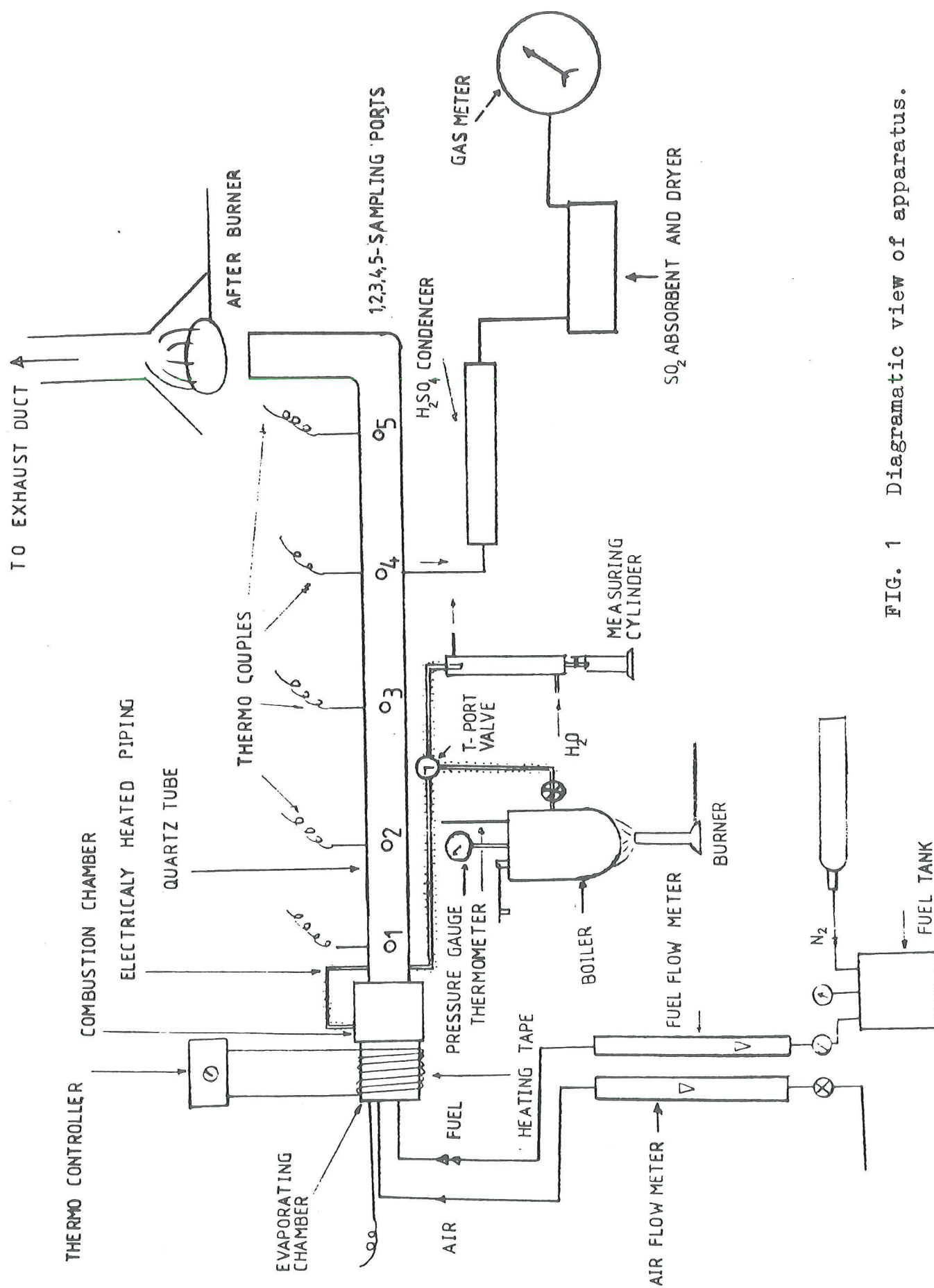


FIG. 1 Diagrammatic view of apparatus.



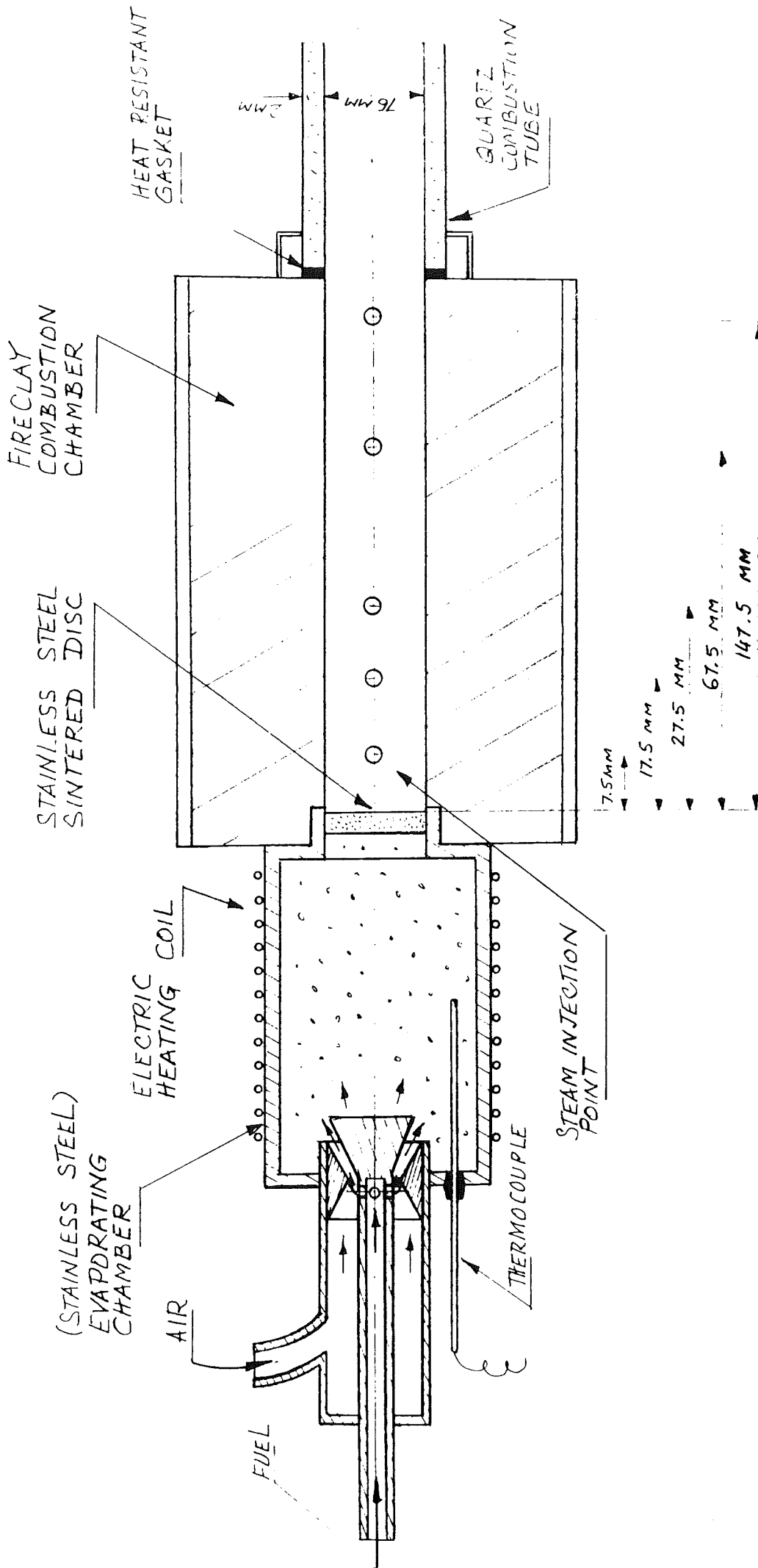


FIG. 2 ATOMISER AND PREMIX EVAPORATING CHAMBER

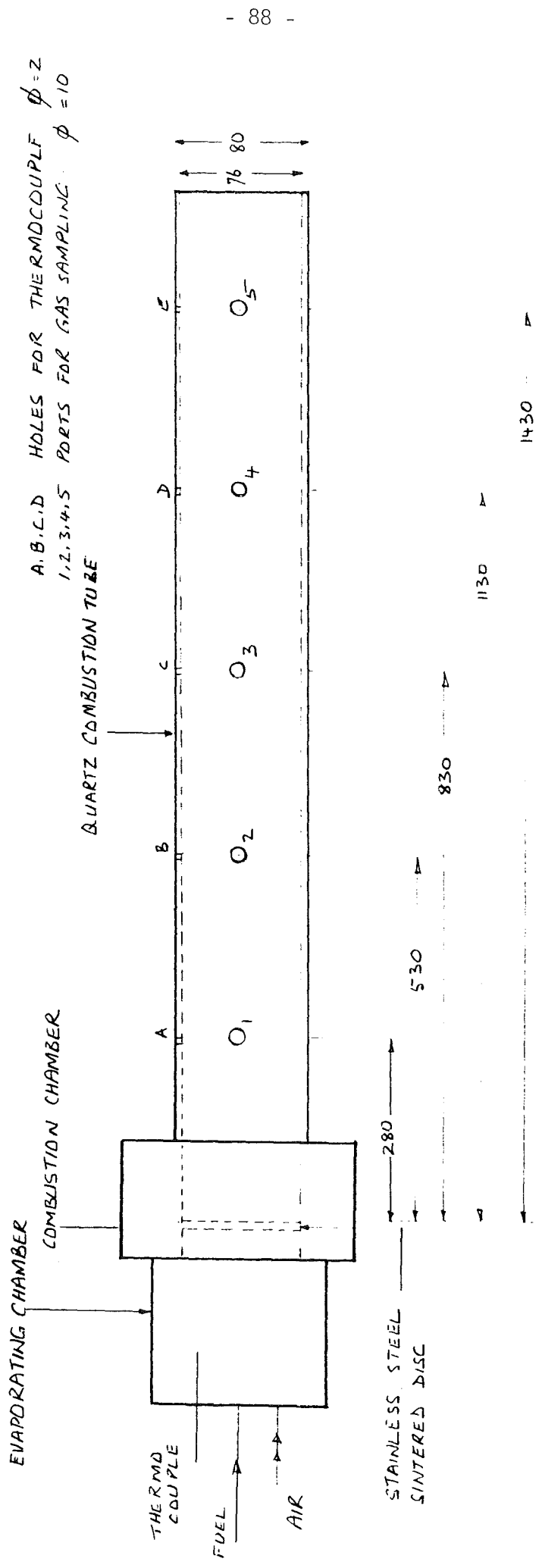


FIG. 3 Combustion system.

DIM IN MM NOT TO SCALE

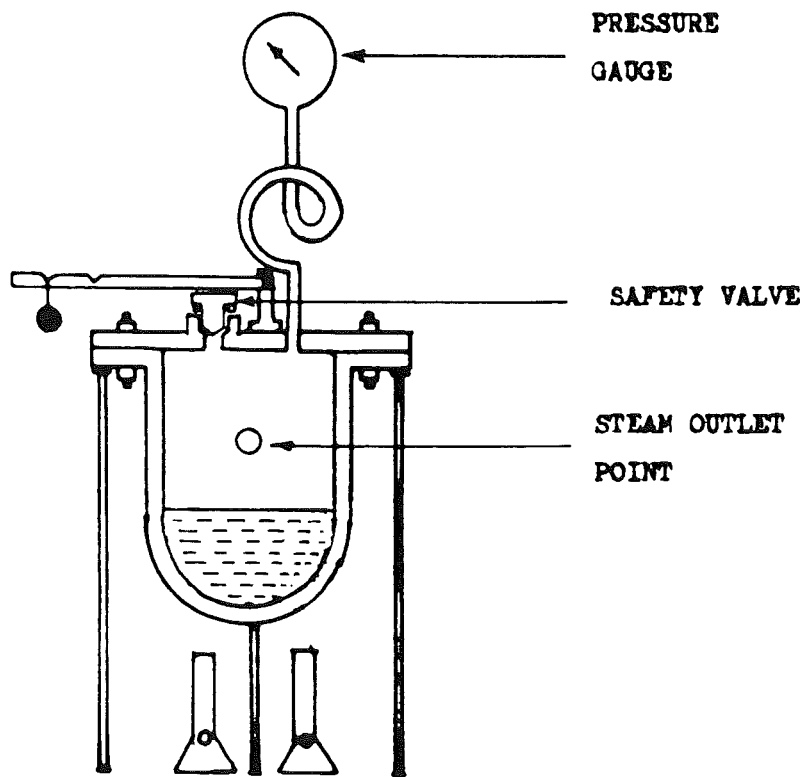


FIG. 4 Boiler for steam injection.

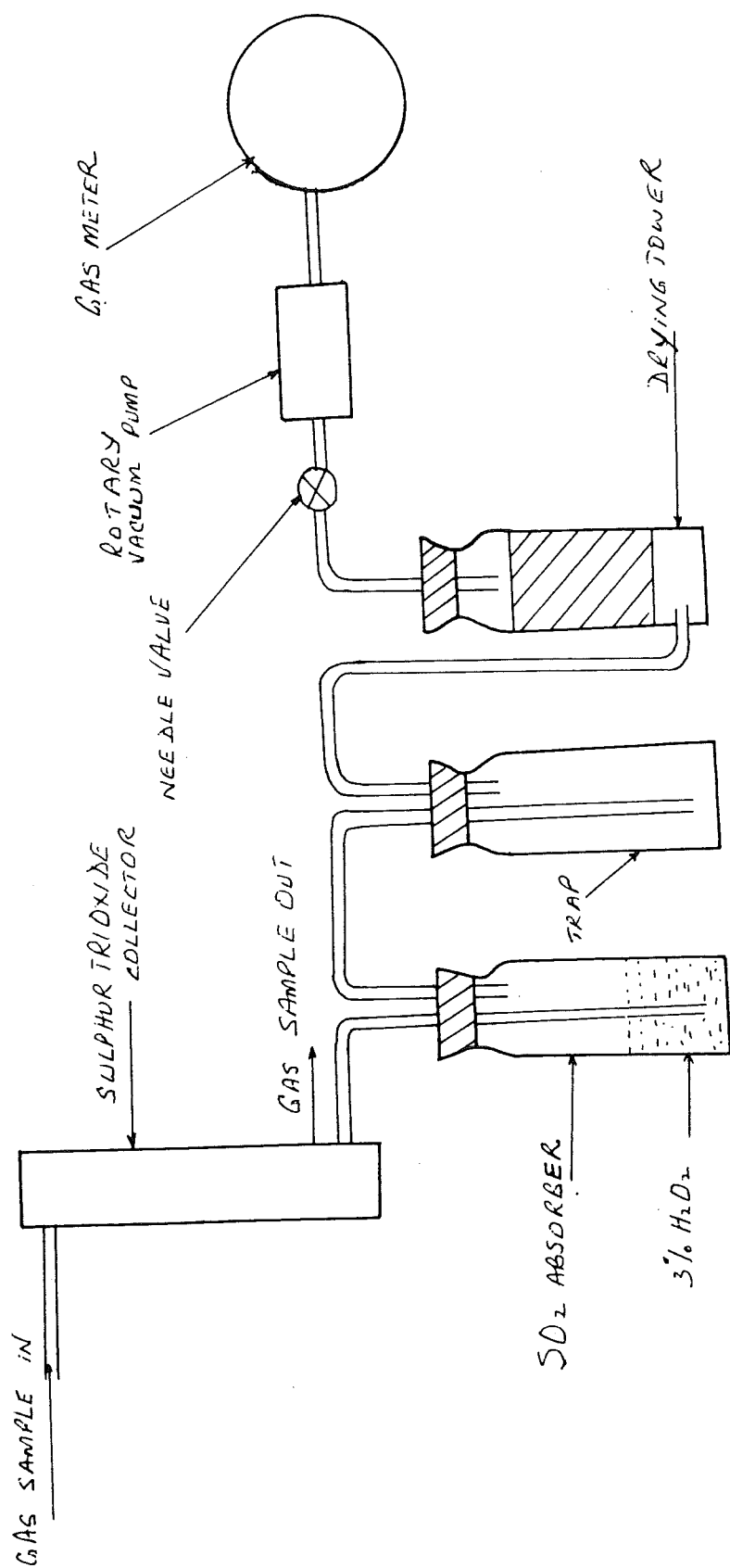


FIG. 5 Sampling train for the extraction of sulphur oxides from flue gases.

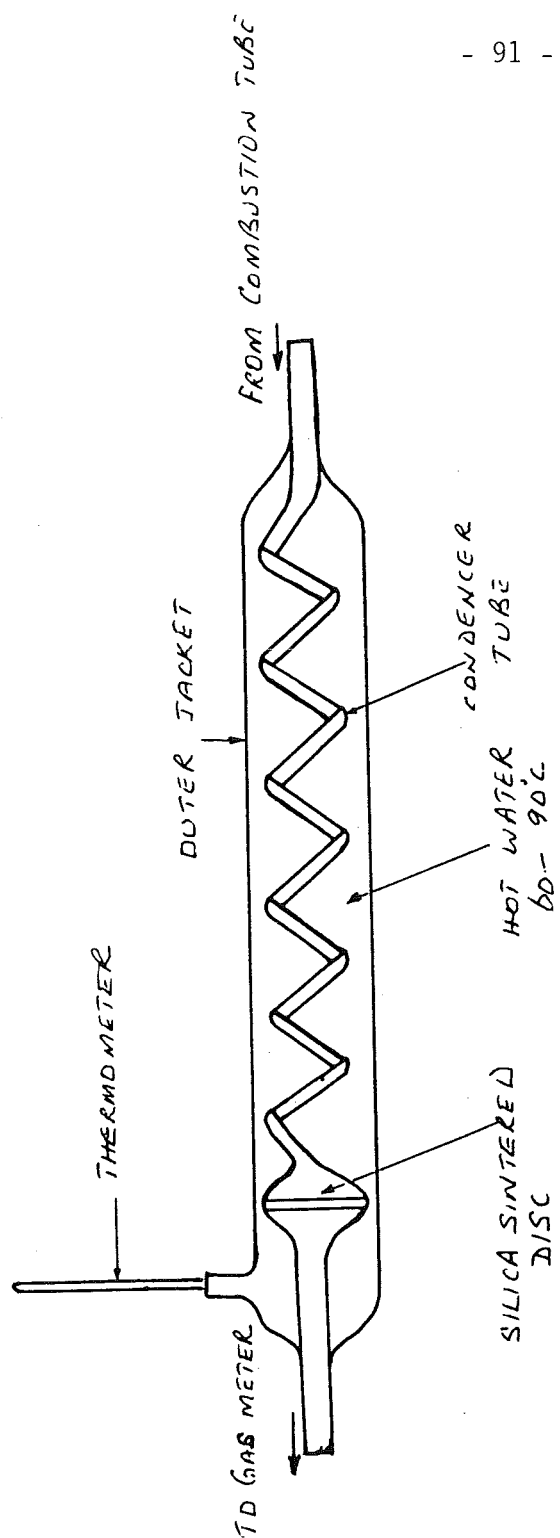
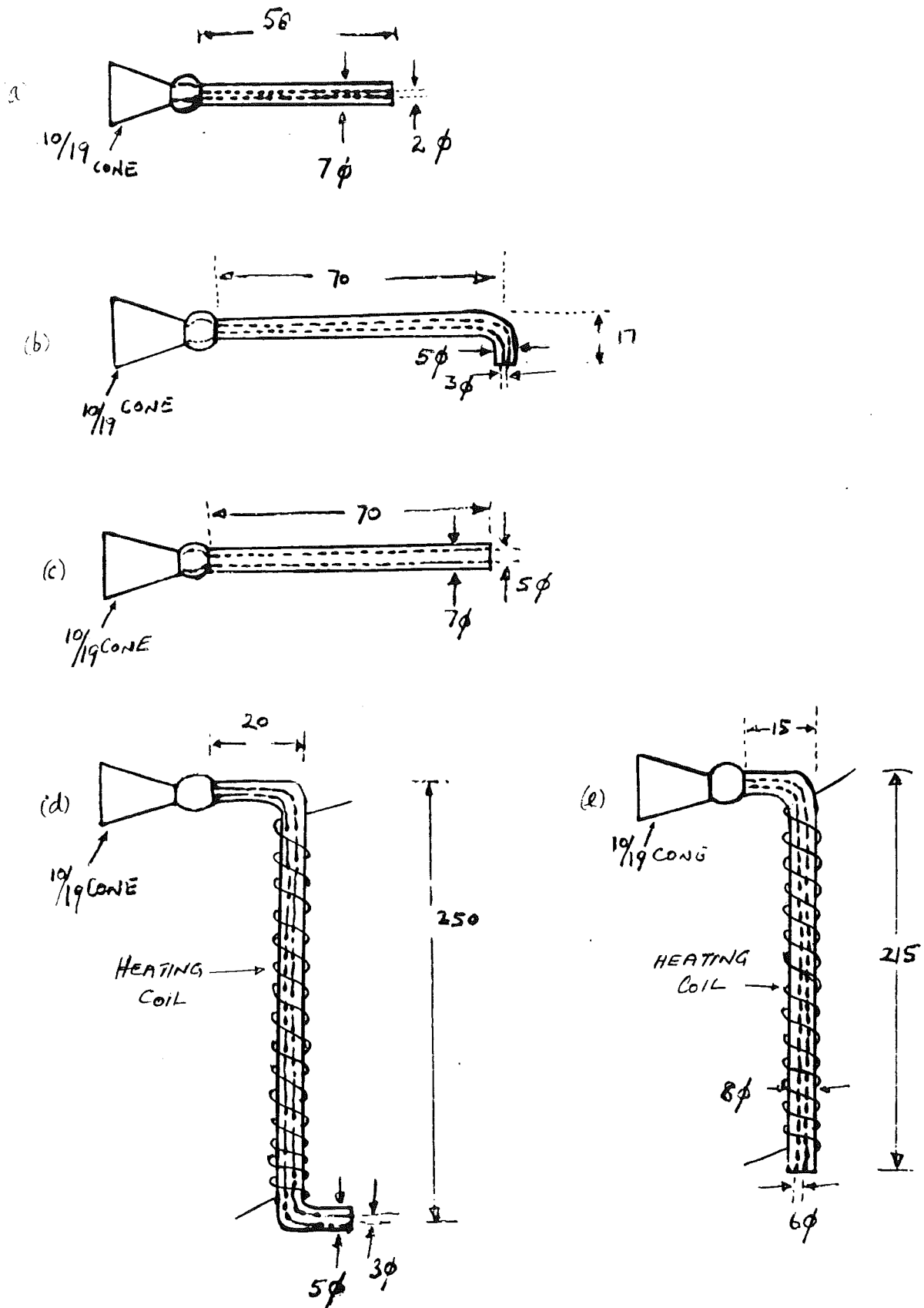


FIG. 6 Sulphur trioxide collector.



MATERIAL - QUARTZ.  
DIMENSIONS IN MM.  
DRAWING NOT TO SCALE

FIG. 7 Gas sampling probes.

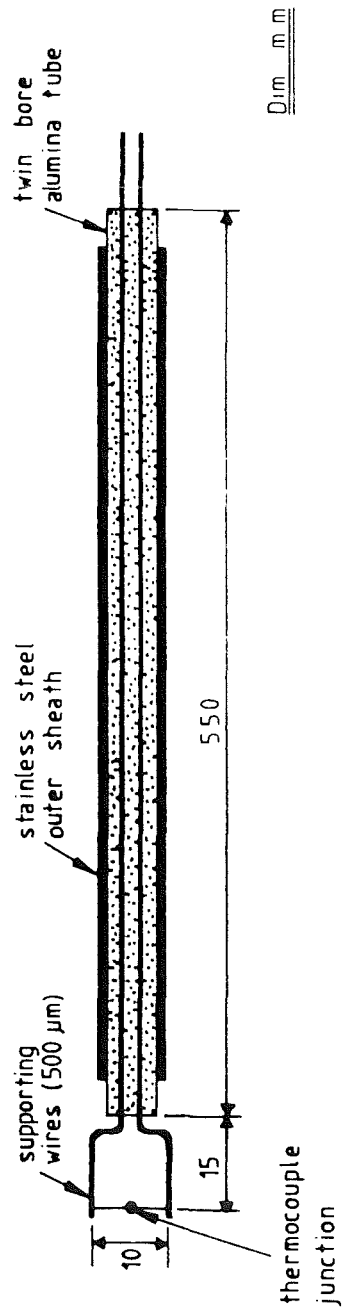


FIG. 8 Details of fine wire thermocouple probe.

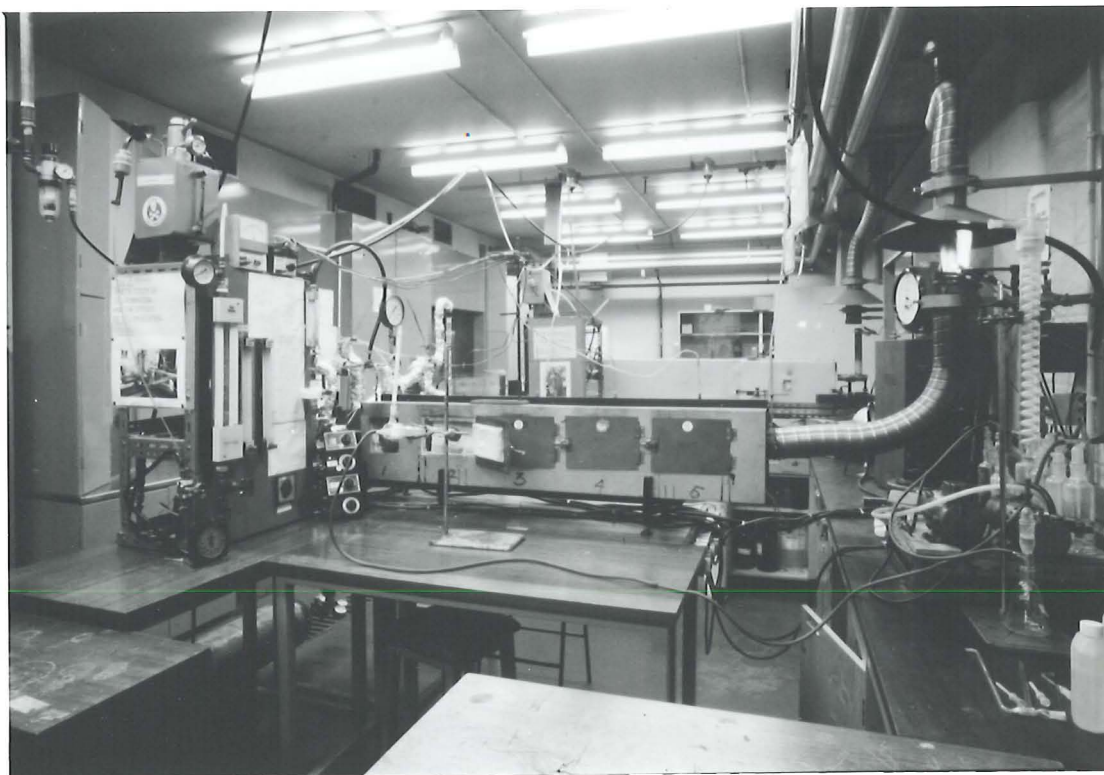


plate (1) Photograph of general appearance of the apparatus.



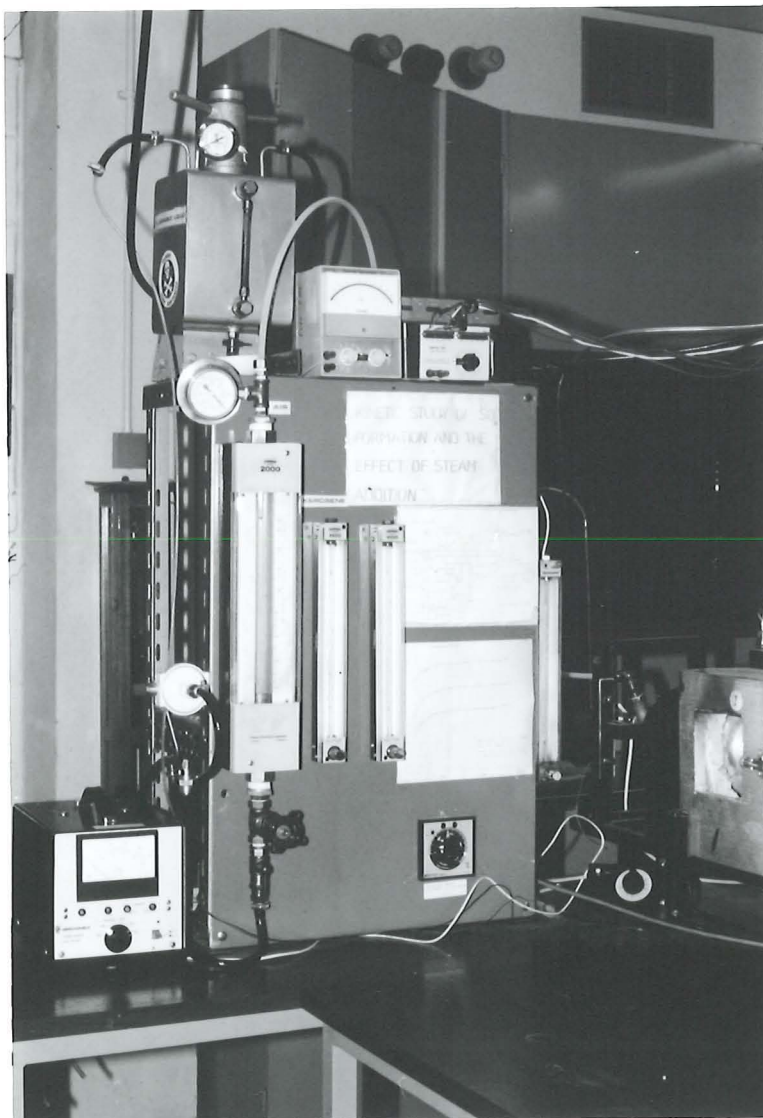


plate (2) Photograph of instrumentation and fuel tank.

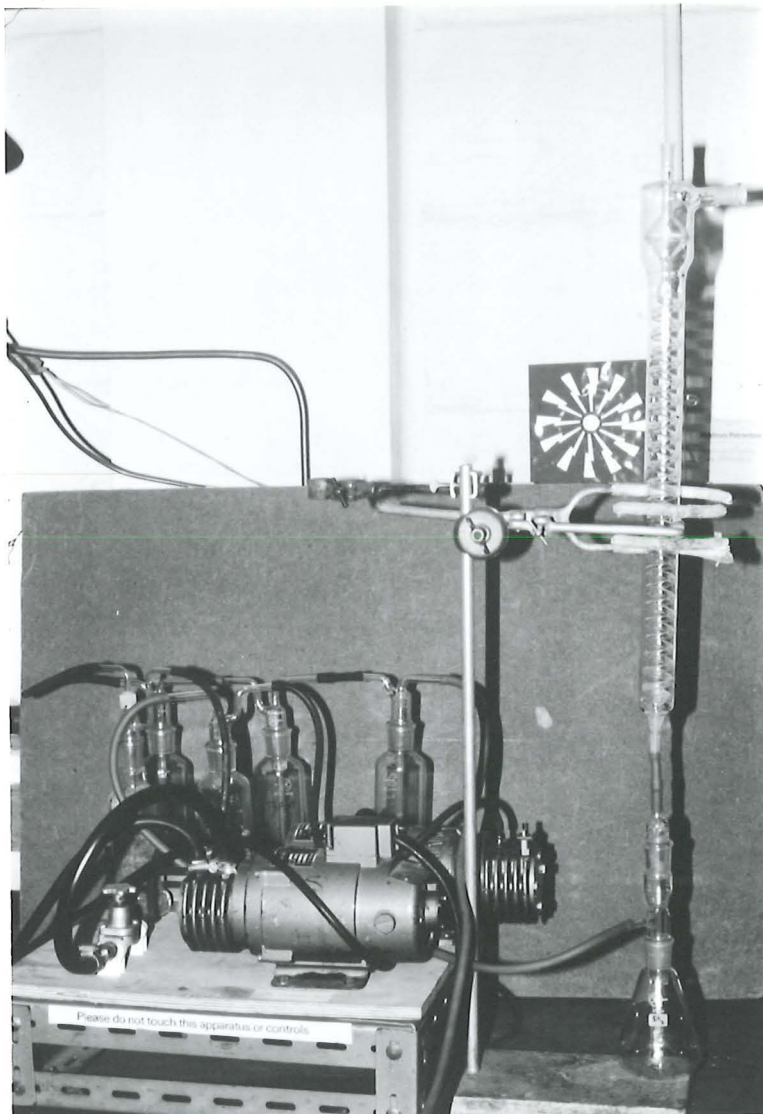


plate (3) Photograph of sampling unit.

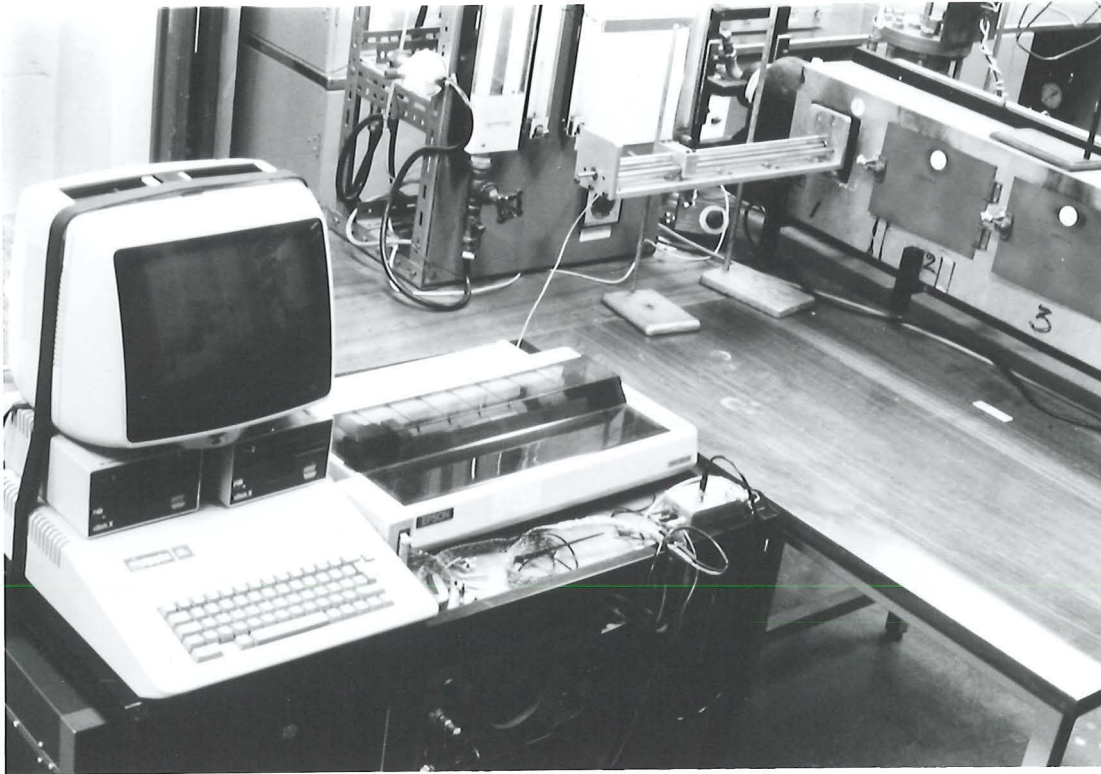


plate (4) Photograph of temperature measuring system.

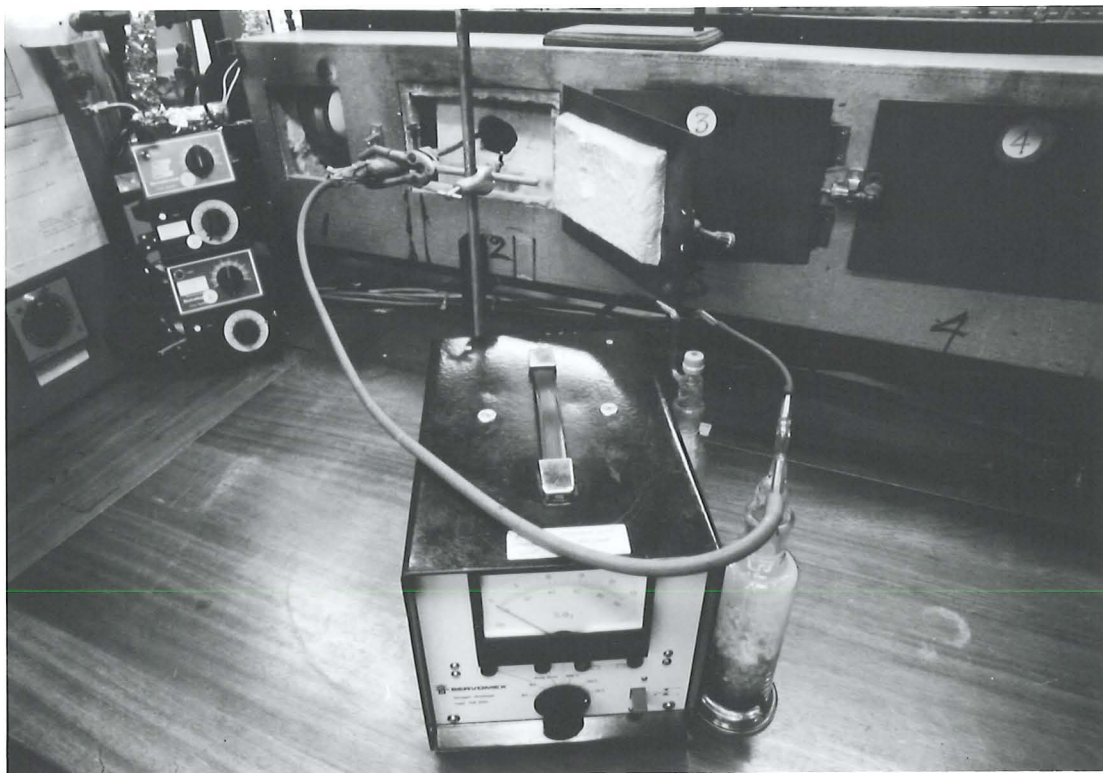


plate (5) Photograph of oxygen analyser in use.

APPENDIX

- I Calculation of the amount of carbon disulphide ( $\text{CS}_2$ ) needed to increase the sulphur content of kerosene by 3.4% (wt).
- II The principle of operation of Servomex  $\text{O}_2$  Analyser.
- III Calculation to show the rate of reaction of  $[\text{CO}]$  with  $[\text{O}]$  is greater than the rate of reaction of  $[\text{SO}_2]$  with  $[\text{O}]$ .
- IV Calculation of Reynolds number.
- V Calculation of air to fuel ratio to obtain 4.5%  $\text{O}_2$ .
- VI Theoretical calculation of the concentration of  $\text{SO}_3$  in flue gases.
- VII Determination of  $\text{SO}_3$  by Goksoyer and Ross method.
- VIII Factors effecting  $\text{SO}_3$  concentration during sampling and determination by Goksoyer and Ross method.
- IX Radiation correction of temperature measured by fine wire thermocouple.
- X FYRITE GAS ANALYSERS  
DESCRIPTION AND OPERATION
- XI Calculation of the velocity of combustion gases at  $550^\circ\text{C}$ .

XII COURSE AND CONFERENCES ATTENDED AND PUBLICATIONS DURING  
THE PRESENT PERIOD OF STUDY.

APPENDIX I

CALCULATION OF THE AMOUNT OF CARBON DISULPHIDE ( $\text{CS}_2$ )  
NEEDED TO INCREASE THE SULPHUR CONTENT OF KEROSENE BY 3.4% (WT)

Assumption: Initially no sulphur is present in the kerosene.

(Density of kerosene 0.783 g/cc, Density of  $\text{CS}_2$  = 1.27 g/cc).

64g of sulphur is present in 76 g of  $\text{CS}_2$  (M wt)

1g of sulphur is present in 1.188 g of  $\text{CS}_2$ .

1.188g of  $\text{CS}_2$  added to 98.812 g of kerosene will give a  
mixture of fuel with 1% s (wt)

4.04 g of  $\text{CS}_2$  added to 95.96 g of kerosene will give a  
mixture of fuel with 3.4% s (wt).

3.18 cc of  $\text{CS}_2$  added to 122.55 cc of kerosene will give a  
mixture with 3.4% s (wt).

$\therefore$  26 cc of  $\text{CS}_2$  added to 1000 cc of kerosene will give a  
mixture with 3.4% s (wt).

## APPENDIX II

### THE PRINCIPLE OF OPERATION OF SERVOMEX O<sub>2</sub> ANALYSER

O<sub>2</sub> is strongly paramagnetic and is unique amongst common gases. Most other gases are weakly diamagnetic apart from Nitric oxide and nitrogen peroxide. So the measurement of the susceptibility provides a specific indication.

All servomex oxygen analysers consist of a light dumb-bell shaped test body which is suspended on a platinum-iridium wire in a non-uniform magnetic field. It experiences a torque proportional to the magnetic susceptibility of the gas surrounding the test body. This torque balanced against a restoring torque due to current flow in a coil wound on the dumb-bell the balance condition being achieved by manual adjustment of a calibrated source to attain the "zero" position of a beam of light reflected from the dumb-bell. The zero position is initially determined by passing oxygen free nitrogen into the measuring cell. Before introducing the sample gas the output dial is set to 6% oxygen by drawing test gas (with 6% oxygen) into the cell and the span is adjusted to give balance. Alternatively air too could be drawn and the dial set at 21% oxygen. Since the device is linear this single adjustment is sufficient to set up the measurement.

The following results for O<sub>2</sub> measurements were obtained along the tube:

4.6, 4.6, 4.5, 4.5, 4.5%.



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mean value for  $O_2 = 4.54\%$

deviation =  $\pm 0.055\%$

percentage error =  $\pm 1.21\%$

### APPENDIX III

CALCULATIONS TO SHOW THE RATE OF REACTION OF [CO] WITH [O]<sup>></sup>

RATE OF REACTION OF [SO<sub>2</sub>] WITH [O]

$$\text{Ratio} = \frac{\text{Rate CO}}{\text{Rate SO}_2} = \frac{K_{\text{CO}} [\text{CO}] [\text{O}] [\text{all gases}]}{K_{\text{SO}_2} [\text{SO}_2] [\text{O}] [\text{all gases}]}$$

Composition of kerosene 85.9% C, 14.1% H (no sulphur initially).

Density of kerosene = 0.783 g/cc, Density of CS<sub>2</sub> = 1.27 g/cc.

26.0 cc of CS<sub>2</sub> added to 1000 cc of kerosene will give 3.4% S in the fuel mixture.

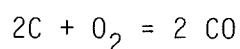
Using densities and initial composition of the fuel the new composition will be as 83.1% C, 3.4% S and 13.5% H approximately.

The density change of the new fuel is assumed to be negligible.

To find [CO].

$$\text{Wt of carbon in 1000 cc (783 g) of fuel} = 783 \times \frac{83.1}{100} = 650.67 \text{ g}$$

It is assumed all carbon in the fuel is first converted to CO



hence one mol of C → 1 mole CO

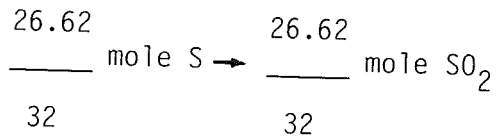
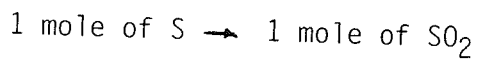
$$\therefore \frac{650.67}{12} \text{ mole of C} \rightarrow \frac{650.67}{12} \text{ mole CO}$$

$$[CO] = 54.22/\text{volumetric flow rate.}$$

To find  $[SO_2]$

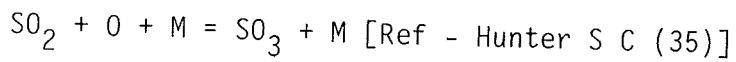
$$\begin{aligned}\text{Wt of sulphur in 1000 cc (783 g) of fuel} &= 783 \times \frac{3.4}{100} \\ &= 26.62 \text{ g}\end{aligned}$$

It is assumed that all sulphur in the fuel is first converted to  $SO_2$ .



$$[SO_2] \rightarrow 0.83/\text{volumetric flow rate}$$

To find  $K_{SO_2}$



$$K_{SO_2} = AT^{-N} \exp\left(\frac{-B}{RT}\right) \quad A = 3.63 \times 10^{14}$$

$$N = 0$$

$$B = -1$$

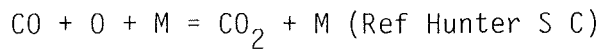
$$T = 1700^\circ\text{C} = 1973 \text{ K assumed}$$

$$R = 0.001987$$

$$K_{SO_2} = 3.63 \times 10^{14} \times 1973^0 \times \exp\left(\frac{1}{0.001987 \times 1973}\right)$$

$$K_{SO_2} = 4.68 \times 10^{14} \text{ (cc /mol) } \text{sc}^{-1}$$

To find  $K_{CO}$



$$K_{CO} = AT^{-N} \exp\left(\frac{-B}{RT}\right) \quad A = 5.10 \times 10^{15}$$

$$N = 0$$

$$B = 3.580$$

$$T = 1700^{\circ}C = 1973K \text{ assumed}$$

$$K_{CO} = 5.1 \times 10^{15} \times 1973^0 \exp\left(\frac{-3.580}{0.001987 \times 1973}\right)$$

$$K_{CO} = 20.46 \times 10^{14} \text{ (CC/mole) } \text{sc}^{-1}$$

$$\text{Ratio} = \frac{\text{Rate CO}}{\text{Rate SO}_2} = \frac{K_{CO} [CO]}{K_{SO_2} [SO_2]}$$

$$= \frac{20.46 \times 10^{14} \times 54.22}{4.68 \times 10^{14} \times 0.83}$$

$$= 2.85 \times 10^2$$

APPENDIX IV

CALCULATION OF REYNOLDS NUMBER

Consider the following operating condition:

fuel: kerosene + 3.4% s (wt)

fuel consumption  $6 \text{ CM}^3 \text{ min}^{-1}$

excess oxygen in combustion gases: 4.5% (v/v)

gas temperature at port 2:  $750^\circ\text{C}$

density of kerosene:  $0.783 \text{ g cm}^{-3}$

It is assumed combustion gases have the properties of air at higher temperatures.

1 kg of kerosene when burned stoichiometrically produces  $12.13 \text{ m}^3$  of combustion gases at NTP (46).

$6 \text{ cm}^3 \text{ min}^{-1}$  kerosene when burned stoichiometrically will

$$\begin{aligned} \text{produce} &= \frac{12.13 \times 0.783 \times 6}{10^3} \text{ m}^3 \text{ min}^{-1} \text{ NTP} \\ &= 57 \times 10^{-3} \text{ m}^3 \text{ min}^{-1} \end{aligned}$$

Theoretical combustion air required for burning 1 kg of kerosene at NTP =  $11.35 \text{ m}^3$  (46).

4.5%  $\text{O}_2$  will be in 22% excess air.

$\therefore$  Actual excess air used during combustion  $6 \text{ cm}^3 \text{ min}^{-1}$  kerosene

$$\begin{aligned} &= 11.35 \times \frac{22}{100} \times 6 \times 10^{-3} \times 0.783 \text{ m}^3 \text{ min}^{-1} \\ &= 11.73 \times 10^{-3} \text{ m}^3 \text{ min}^{-1} \text{ at NTP} \end{aligned}$$

$\therefore$  Total volume of combustion gases produced when burned  $6 \text{ CM}^3 \text{ min}^{-1}$  kerosene

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$$= 68.73 \times 10^{-3} \text{ m}^3 \text{ min}^{-1} \text{ NTP}$$

Volume of  $68.73 \times 10^{-3} \text{ m}^3$  of gases at  $750^\circ\text{C}$

$$= 257.5 \times 10^{-3} \text{ m}^3$$

Maximum Velocity of gases at  $750^\circ\text{C}$

$$= \frac{257.5 \times 10^{-3} \times 2}{\pi/4(7.6)^2 \times 10^{-4} \times 60} \text{ ms}^{-1}$$

$$= 1.9 \text{ ms}^{-1}$$

$$\text{Re} = \frac{Vd}{\Delta}$$

where V = velocity of gases

d = diameter

$\Delta$  = kinematic viscosity

at  $750^\circ\text{C}$   $\Delta = 1.25 \text{ cm}^2 \text{ s}^{-1}$  (46)

$$\therefore \text{Re} = \frac{1.9 \times 10^2 \times 7.6}{1.25}$$

$$= 1155.$$

This figure is less than 2000. Thus the flow is determined to be laminar.

APPENDIX V

CALCULATIONS OF AIR TO FUEL RATIO TO OBTAIN 4.5%  $O_2$

Initial composition of kerosene was given as

C = 85.9%, H = 14%, S = 0.08% (by weight) (46).

Density of kerosene = 0.783 g/cc at 20°C

Density of air = 1.2928 g/lit at 20°C

Composition of volumetric air  $O_2$  - 21%,  $N_2$  = 79%

Composition of gravimetric air  $O_2$  - 23.3%,  $N_2$  = 76.7%

By addition of  $CS_2$  to kerosene to a mass ratio of 0.04:1

the chemical composition will be

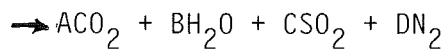
C = 83.1% S = 3.4% H = 13.5% by weight (from calculations, approximately).

As a first approximation it was assumed that complete combustion takes place and all the sulphur was converted to  $SO_2$  and that  $N_2$  did not take part in the reaction.

Consider 1 kg of fuel reacting stoichiometrically with X kg of air.

The combustion equation in kmole will be

$$\frac{0.831C}{12} + \frac{0.135H}{1} + \frac{0.034S}{32} + X\left(\frac{0.233}{32}O_2 + \frac{0.767}{28}N_2\right)$$



Now by a molar balance

$$A = \frac{0.831}{12} = 0.069$$

$$B = \frac{0.135}{2} = 0.0675$$

$$C = \frac{0.034}{32} = .0011$$

$$2X \left( \frac{0.233}{32} \right) = 2A + B + 2C$$

$$= 2 \times 0.069 + 0.0675 + 2 \times 0.0011$$

$$X = 14.3$$

Hence AIR/FUEL ratio = 14.3 by mass

ie 1 g of fuel requires 14.3 g of air for stoichiometric combustion

$$\therefore \frac{1}{0.783} \text{ cc fuel requires } \frac{14.3}{1.2928} \text{ liters of air}$$

$\therefore$  at stoichiometric combustion 1 cc of fuel needs 8.662 liters of air (8662 cc air)

By volumetric analysis of air

$$4.5 \text{ cc } O_2 \text{ will be present in } \frac{100}{21} \times 4.5 \text{ cc air}$$

$$= 21.43 \text{ cc air}$$

$\therefore$  21.43% of excess air added to the combustion will give 4.5% excess  $O_2$  in flue gases (by volume).

$\therefore$  at 4.5% excess  $O_2$  the volume of air required for 1 cc

$$\text{of fuel is } 8.662 + \left( 8.662 \times \frac{21.43}{100} \right) \text{ liters}$$

$$= 10.5183 \text{ liters.}$$



# APPENDIX VI

## THEORETICAL CALCULATION OF THE CONCENTRATION OF $\text{SO}_3$ IN FLUE GASES

Data:

Temperature of gases at sampling point =  $750^\circ\text{C} = 1023 \text{ K}$

Distance of sampling point from origin of flame = 58 cm

Excess  $\text{O}_2$  in flue gases = 4.5%

Internal diameter of combustion tube = 76 mm

Fuel consumption =  $6 \text{ cm}^3 \text{ m}^{-1}$

Density of fuel (kerosene) =  $0.783 \text{ g cm}^{-3}$

Air input to obtain 4.5%  $\text{O}_2$  =  $63.1 \text{ lit min}^{-1}$  (calculated approx)

Combustion gases produced at NTP =  $69 \text{ lit min}^{-1}$  (calculated approx).

Mean relative molecular mass of air = 29

Density of air =  $1.29 \text{ g lit}^{-1}$  (NTP)

Density of  $\text{CO}_2$  =  $1.828 \text{ g lit}^{-1}$  (NTP)

Density of  $\text{O}_2$  =  $1.324 \text{ g lit}^{-1}$  (NTP)

Density of  $\text{CS}_2$  =  $1.27 \text{ g cm}^{-3}$

$$[\text{SO}_3]^1 = \int_{x=0}^{x=1} \frac{A[\text{O}_2][\text{SO}_2]}{VxRTx} \exp\left[\frac{-B}{Tx}\right] dx \quad (\text{ref 11})$$

where  $A = 2.6 \left( \pm 1.3 \right) \times 10^{12} \text{ mole}^{-1} \text{ cm}^3 \text{ s}^{-1}$

$B = 23,000 \pm 1200 \text{ K}$

$[\text{SO}_3]$ ,  $[\text{O}_2]$ ,  $[\text{SO}_2]$  are partial pressures

### Assumptions

- (i) No major change takes place to the pressure of the system. Hence, equal to atmospheric.
- (ii) All sulphur in the fuel converted to  $\text{SO}_2$ .
- (iii)  $\text{N}_2$  does not take part in any reaction.
- (iv) No loss of mass in the system.
- (v) It is assumed a positive change in A and B according to each degree of increase in temperature from 900K  
∴ at 1023 K     $A = 2.954 \times 10^{12}$  (change  $2.88 \times 10^{-3} \text{K}^{-1}$ )  
                   $B = 23327$             (change  $2.66 \text{K}^{-1}$ )
- (vi) Combustion gases behave like air.

$$1000 \text{ cm}^3 \text{min}^{-1} \text{ fuel mixture contains } = 974 \text{ cm}^3 \text{min}^{-1} \text{ kerosene}$$

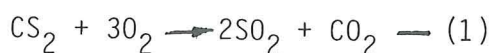
(from Appendix I)

$$\begin{aligned} 6 \text{ cm}^3 \text{min}^{-1} \text{ fuel mixture contains} &= \frac{974}{1000} \times 6 \text{ cm}^3 \text{min}^{-1} \text{ kerosene} \\ &= 5.84 \text{ cm}^3 \text{min}^{-1} \end{aligned}$$

$$\begin{aligned} \therefore \text{Volume of CS}_2 \text{ in } 6 \text{ cm}^3 \text{min}^{-1} \\ \text{of fuel mixture} &= 6 - 5.84 \text{ cm}^3 \text{min}^{-1} \\ &= 0.16 \text{ cm}^3 \text{min}^{-1} \end{aligned}$$

$$\therefore \text{mass flow rate of CS}_2 = \frac{0.16 \times 1.27}{60} \text{ gs}^{-1}$$

$$\begin{aligned} \therefore \text{moles of CS}_2 &= \frac{0.16 \times 1.27}{60 \times 76} \text{ moles}^{-1} \\ &= 4.46 \times 10^{-5} \text{ moles}^{-1} \end{aligned}$$



$4.46 \times 10^{-5} \text{ moles}^{-1}$  of  $\text{CS}_2$  will produce

$$4.46 \times 10^{-5} \times 2 \text{ moles}^{-1} \text{ of SO}_2 = 8.92 \times 10^{-5} \text{ moles}^{-1}$$

$$\therefore \text{mass flow rate of SO}_2 = 8.92 \times 10^{-5} \times 64 \text{ gs}^{-1}$$

$$\begin{aligned} M_{\text{SO}_2} &= 5.71 \times 10^{-3} \text{ gs}^{-1} \end{aligned}$$

$$\begin{aligned} \text{mass of air supplied} &= \frac{63.1 \times 1.29}{60} \text{ gs}^{-1} \end{aligned}$$

$$= 1.35 \text{ gs}^{-1}$$

$$\begin{aligned}
 \text{mass of } N_2 \text{ in air supplied} &= 1.35 \times \frac{76.7}{100} \text{ gs}^{-1} \\
 M_{N_2} &= 1.035 \text{ gs}^{-1} \\
 \text{Moles of } N_2 &= \frac{1.035}{28} \text{ gs}^{-1} \\
 &= 36.96 \times 10^{-3} \text{ moles}^{-1}
 \end{aligned}$$

1 kg of kerosene produces  $12.13 \text{ m}^3$  of combustion gases at NTP when burned stoichiometrically (46)

$$\begin{aligned}
 \text{Kerosene flow rate} &= 5.84 \text{ cm}^3 \text{ min}^{-1} \\
 \text{mass flow rate of kerosene} &= \frac{5.84}{60} \times 0.783 \text{ gs}^{-1} \\
 &= 0.0762 \text{ gs}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 1 \text{ g of kerosene produces} &12.13 \text{ lit gases} \\
 \therefore 0.0762 \text{ gs}^{-1} \text{ kerosene produces} &12.13 \times 0.0762 \\
 &= 0.924 \text{ ls}^{-1}
 \end{aligned}$$

$\text{CO}_2$  in exhaust gases = 13.2% during stoichiometric combustion (46)

$$\begin{aligned}
 \therefore \text{CO}_2 \text{ in } 0.924 \text{ ls}^{-1} \text{ gases} &= 0.924 \times \frac{13.2}{100} \text{ ls}^{-1} \\
 \therefore \text{mass of CO}_2 \text{ from kerosene} &= 0.924 \times \frac{13.2}{100} \times 1.828 \text{ gs}^{-1} \\
 &= 0.223 \text{ gs}^{-1} \\
 \therefore \text{moles of CO}_2 \text{ from kerosene} &= \frac{0.223}{44} \\
 &= 5.068 \times 10^{-3} \text{ moles}^{-1}
 \end{aligned}$$

$$\text{CS}_2 \text{ supplied during combustion} = 4.46 \times 10^{-5} \text{ moles}^{-1}$$

From (1) 1 mole of  $\text{CS}_2$  will produce 1 mole of  $\text{CO}_2$

$$\therefore \text{CO}_2 \text{ produced from CS}_2 = 4.46 \times 10^{-5} \text{ moles}^{-1}$$

$$\therefore \text{total moles of CO}_2 \text{ produced} = 5.11 \times 10^{-5} \text{ moles}^{-1}$$

Combustion gases produced when burned

$$6 \text{ cm}^3 \text{ min}^{-1} = 69 \text{ lit min}^{-1}$$

$$\therefore \text{Mass of O}_2 \text{ in gases} = \frac{69}{60} \times \frac{4.5}{100} \times 1.324 \text{ gs}^{-1}$$

$$M_{\text{O}_2} = 6.85 \times 10^{-2} \text{ gs}^{-1}$$

$$\text{moles of O}_2 = \frac{6.85 \times 10^{-2}}{32}$$

$$= 2.14 \times 10^{-3} \text{ moles}^{-1}$$

Combustion gas contains  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$  and some  $\text{H}_2\text{O}$  vapour

$$\therefore \text{mass of combustion gases} = \frac{69 \times 1.29}{60} \text{ gs}^{-1}$$

$$M_{\text{gas}} = 1.4835 \text{ gs}^{-1}$$

$$\begin{aligned} \therefore \text{mass of H}_2\text{O} &= M_{\text{gas}} - M_{\text{SO}_2} - M_{\text{CO}_2} - M_{\text{N}_2} - M_{\text{O}_2} \\ &= 1.4835 - [5.71 \times 10^{-3} + 5.11 \times 10^{-3} \times 44 \\ &\quad + 1.035 + 6.85 \times 10^{-2}] \\ &= 0.1495 \text{ gs}^{-1} \end{aligned}$$

$$\text{moles of H}_2\text{O} = 8.3 \times 10^{-3} \text{ moles}^{-1}$$

$$\begin{aligned}\therefore \text{Total moles of gases} &= \text{moles}[\text{SO}_2 + \text{CO}_2 + \text{N}_2 + \text{O}_2 + \text{H}_2\text{O}] \\ &= [8.92 \times 10^{-5} + 5.11 \times 10^{-3} + 36.96 \times 10^{-3} \\ &\quad + 2.14 \times 10^{-3} + 8.3 \times 10^{-3}] \\ &= 52.6 \times 10^{-3} \text{ moles}^{-1}\end{aligned}$$

partial pressure of  $\text{SO}_2$

$$= \frac{8.92 \times 10^{-5}}{52.6 \times 10^{-3}} \times 1$$

$$p[\text{SO}_2] = 1.7 \times 10^{-3}$$

$$\begin{aligned}p[\text{O}_2] &= \frac{2.14 \times 10^{-3}}{52.6 \times 10^{-3}} \times 1 \\ &= 40.68 \times 10^{-3}\end{aligned}$$

$$\begin{aligned}[\text{SO}_3]_0^{58} &= \int_0^{58} \frac{2.94 \times 10^{12} \times 40.68 \times 10^{-3} \times 1.7 \times 10^{-3} \times 58}{1.9 \times 100 \times 8.3143 \times 1023} e^{-\left[\frac{2.3327}{1023}\right]} \\ &= 9.12 \times 10^{-7} \text{ moles}^{-1}\end{aligned}$$

1 mole of gases at NTP contains 22.4 lit

$$\therefore 52.6 \times 10^{-3} \text{ gases at NTP contains} = 22.4 \times 52.6 \times 10^{-3} \text{ lit}$$

$$\begin{aligned}\therefore \text{at } 1023 \text{ K} &= \frac{22.4 \times 52.6 \times 10^{-3} \times 1023}{.273} \\ &= 4.415 \text{ ls}^{-1}\end{aligned}$$

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$$9.12 \times 10^{-7} \text{ moles gases at NTP} = 22.4 \times 9.12 \times 10^{-7} \text{ lit}$$

$$\therefore \text{ at } 1023 \text{ k} = \frac{22.4 \times 9.12 \times 10^{-7} \times 1023}{273}$$

$$= 7.655 \times 10^{-5} \text{ lits}^{-1}$$

$$4.415 \text{ lits}^{-1} \text{ gas contains } 7.655 \times 10^{-5} \text{ lits}^{-1} \text{ SO}_3 \text{ at } 1023\text{k}$$

$$\therefore 10^6 \text{ lits}^{-1} \text{ gas contains } \frac{7.655 \times 10^{-5}}{4.415} \times 10^6$$

$$= 17 \text{ ppm}$$

## APPENDIX VII

### GOKSOYER AND ROSS METHOD

#### 1. Scope

This method describes a simplified procedure for the rapid determination of sulphur trioxide in the combustion gases from appliances burning fuels containing sulphur. At the same time sulphur dioxide may also be determined.

Experimental evidence has shown that recovery of sulphur trioxide is for all practical purposes 100%.

#### 2. Method Summary

A measured volume of hot flue gases is drawn through a glass coil and a Grade 4 sintered glass disc, both enclosed in a glass jacket filled with water, maintained at a temperature between 60 and 90°C. This temperature range is sufficiently below the acid dew point to leave a negligible quantity of sulphuric acid in the vapour phase, but high enough to prevent condensation of water vapour. Thus practically all the sulphuric acid condenses on the walls of the coil. Any acid particles left in the gas stream are retained by the sintered glass filter. The acid is then washed out with water and titrated with standard sodium hydroxide solution.

#### 3. Apparatus

The complete sampling train is shown in Figure 5 and consists of the apparatus described in section (a) to (i) below



(a)  $\text{SO}_3$  collector

The  $\text{SO}_3$  collector, suitable for use in laboratory conditions is shown diagrammatically in Figure 3.

Note 1. A more robust version of the collector 1 has been devised for use in industrial plants.

(b) Sampling tube

The choice depends on the position of sampling

(i) Short tube:- Short length of pyrex or quartz tube fitted at one end with the appropriate spherical joint.

(ii) Long tube:- glass sampling line provided with heating to maintain the gas sample at a temperature not below  $250^\circ\text{C}$  during its passage through the line. "Electrothermal" heating tapes around the line can be used or alternatively hot flue gases can be drawn through an outer annulus whilst the sample is drawn through the inner line.

Note 2. If the flue gases are at a high temperature ( $800 - 1000^\circ\text{C}$ ), narrow bore tubing must be used to reduce the residence time at this temperature and so avoid oxidation of  $\text{SO}_2$  during sampling.

(c) Solids filter

A plug of silica wool in the sampling tube to remove solid particles from the sample.

Note 3. Soda-lime glass wool should not be used because of its reaction with  $\text{SO}_3$ .

(d) Absorber for  $\text{SO}_2$

$\text{SO}_2$  is scrubbed out of the gas sample by bubbling through 100 ml of 3% hydrogen peroxide solution neutral to bromophenol blue contained in a tall Dreschel bottle, 250 ml. The B24 head is fitted with a Grade 1 sintered glass disc to break up the gas bubbles.

(e) Trap

A Dreschel bottle, 125 ml to trap any solution that may be blown out of the  $\text{SO}_2$  absorber.

(f) Drying tower

Moisture is prevented from entering the pump by a small drying tower filled with self-indicating silica gel.

(g) Flow control

1/4 inch needle valve (Newman Hender & Co Ltd).

(h) Rotary vacuum pump

Edward's "Speedivac" combined compressor and vacuum pump.  
Model RBF1 or RBF3.

(i) Gas meter

Parkinson and Cowan Laboratory Gas Meter Type E40.  
(2.5 litre capacity per revolution), connected to the outlet side of the pump.

(j) Flasks for washing

Conical flasks, 100 ml fitted with a B24 socket and a B24 Dreschel bottle head.

(k) Funnel

Conical funnel, top diameter 10 cm connected to the appropriate spherical joint with rubber tubing.

(l) Burettes

10 ml micro-burette, Grade A and 50 ml burette, Grade A.

(m) Clips for spherical joints

Type "JC9/18".

4. Reagents

(a) Washing solution consisting of a mixture at pH4.6 of distilled water, 5% by volume of isopropanol (IPA) and bromophenol blue indicator (2 drops per 50 ml solution).

Note 4. This mixture can be made up in large batches and the pH adjusted to pH4.6 by the addition of a small amount of sulphuric acid followed by neutralization with sodium hydroxide solution.

(b) Sodium hydroxide solutions (N/10 and N/50)

Standardize against sulphuric acid using bromophenol blue indicator

(c) Bromophenol blue indicator

Dissolve 0.5 g of solid bromophenol blue in 1 litre of 20% ethanol in water.

(d) Hydrogen peroxide (3%) plus bromophenol blue indicator (2 drops per 50 ml) at PH4.6

, (e) Self-indicating silica gel.

(f) Acetone

(g) Silica wool

(h) Silicone High Vacuum Grease

## 5. Procedure

### (A) Sampling

(a) Ensure that the spiral tube and filter of the  $\text{SO}_3$  collector are clean and dry. To dry these parts, draw acetone and the air through the collector. If the filter disc becomes contaminated with solid particles which have passed through the silica wool filter, clean it with chromic acid. However, all traces of chromic acid must be washed out before the collector is used.

(b) Connect up the sampling train as shown in Figure 2. Ensure that all joints are gas-tight; use silicone grease where necessary.

(c) Allow the appropriate sampling tube to attain a temperature of about  $250^{\circ}\text{C}$ .

Note 5. The flue gases must be maintained above the acid dewpoint temperature before they reach the  $\text{SO}_3$  collector. It is, therefore, important to choose the sampling tube carefully (Section (3b)).

(d) Fill the outer jacket of the  $\text{SO}_3$  collector with water at a temperature of  $60\text{--}90^{\circ}\text{C}$ .

Note 6. The water must not be allowed to cool below  $60^{\circ}\text{C}$  during the sampling period. The temperature may be maintained by

- (i) Sampling the hot gases at a sufficiently high rate.
  - (ii) insulation of the collector.
  - (iii) electrical heating of water.
  - (iv) circulation of hot water from a thermostatically controlled bath.
- (e) Close the needle valve, start the pump and read the gas meter.
- (f) Open the needle valve and draw flue gases through the sampling train at a rate of up to 5/10 l/min. When the appropriate volume of gas has been sampled, close the needle valve.

Note 7. The volume of gas sampled may be varied according to the concentration of  $\text{SO}_3$ , so that a reasonable titration value is always obtained. This is illustrated by the following example:-

25 litres of gas at  $25^\circ\text{C}$  containing 50 ppm  $\text{SO}_3$  will need 5.1 ml N/50 NaOH  
100 litres of gas at  $25^\circ\text{C}$  containing 5 ppm  $\text{SO}_3$  will need 2.04 ml N/50 NaOH.

- (g) Disconnect the sampling line and draw a small quantity of air through the sampling train. Switch off the pump.

(B) Determination of sulphur trioxide

- (a) Remove the  $\text{SO}_3$  collector and connect the funnel to the inlet and a washing flask to the outlet.

- (b) Pour 50 ml of washing solution into the funnel and carefully draw it by suction through the collector and into the flask.
- (c) Remove the flask and titrate the contents with standard N/50 sodium hydroxide solution from a micro burette until the blue end point is reached.
- (d) To ensure that all the sulphuric acid has been removed, draw the neutralized washing once again through the collector.

(C) Determination of sulphur dioxide

- (a) Remove the sulphur dioxide absorber, add 1-2 drops of bromophenol blue indicator and titrate the contents with standard N/10 sodium hydroxide solution from a 50 ml burette, until the blue end point is reached.

6. Calculation

Calculate the  $\text{SO}_2$  and  $\text{SO}_3$  contents by means of the following equation:-

$$\frac{\text{SO}_2 \text{ or } \text{SO}_3 \text{ ppm by volume of dry gas}}{V} = \frac{T \times N \times 11.2 \times 10^6}{V}$$

Where T = Titration Value, ml

N = Normality of NaOH solution

V = Volume sampled, cc of dry flue gas corrected to  $0^\circ\text{C}$  and 760 mm HG.

7. Example - results obtained from one experiment with the silica tube.

temperature of gas at gas meter end  $20^{\circ}\text{C}$

volume of gas sampled 100 literes

titration value of NaOH 12.6 ml

normality of NaOH 0.02 N

It is assumed that the pressure change in the system is negligible.

$\therefore$  The corrected volume of gas sampled V

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}, \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}, \quad \frac{100}{293} = \frac{V}{273}$$

$$V = 93.2 \text{ literes}$$

by substituting the results in equation for  $\text{SO}_3$

$$\begin{aligned} \text{SO}_3 &= \frac{12.5 \times 0.02 \times 11.2 \times 10^6}{93.2 \times 10^3} \\ &= 30.28 \end{aligned}$$

$\therefore \text{SO}_3$  by volume of dry gas = 30.0 ppm

The following results for  $\text{SO}_3$  measurements were obtained at Port 2 in an earlier case with the silica tube. The air fuel ratio and all other parameters remained constant.

31, 29, 29, 29, 31, 30, 31, 29, 27, 27 ppm

$\therefore$  mean value for  $\text{SO}_3$  = 29 ppm

deviation =  $\pm 1.5$  ppm

percentage error =  $\pm 5.17\%$ .

## APPENDIX VIII

### FACTORS EFFECTING $\text{SO}_3$ CONCENTRATION DURING SAMPLING AND DETERMINATION BY GOKSOYER AND ROSS METHOD

#### 1. Excess oxygen:

Excess oxygen in flame gases to be kept constant during sampling. Hence  $\text{O}_2\%$  in flame gases was measured every time before sampling.

#### 2. Temperature of gases:

The temperature of the gases was measured before and after the gas samples were taken. Throughout the experiment the temperatures were maintained fairly steady.

#### 3. Sulphur content of fuel:

$\text{SO}_3$  increases with the sulphur content of the fuel. It was made sure that every time fuel was prepared exact amount of  $\text{CS}_2$  was added to exactly measured kerosene.

#### 4. The material of combustion chamber and tube:

The material of the combustion chamber and tube could influence the formation of  $\text{SO}_3$ . It has been shown that mild steel catalyses  $\text{SO}_2$  oxidation above  $600^\circ\text{C}$ . In order to avoid catalytic effect in oxidation of  $\text{SO}_2$ , quartz tube was used.

#### 5. Temperature of the sampling probe:

The temperature of the sampling probe must be above the acid dew point of the  $\text{H}_2\text{SO}_4$  vapour otherwise  $\text{SO}_3$  vapour may condense in the sampling tube itself. The probe temperature has to be kept above  $250^\circ\text{C}$  to prevent acid condensation in the probe.



6. The material of probe:

The material of probe should be a non catalyser of  $\text{SO}_2$  oxidation. In this experiment a quartz short probe was used. This eliminated the question of catalysing and condensing in the probe.

7. Temperature of the condenser:

The temperature of the condenser tube should be kept between  $60^\circ$  and  $90^\circ$  to enable  $\text{H}_2\text{SO}_4$  vapour to condense and to allow  $\text{SO}_2$  vapour to escape to the bubbling dreschel bottle.

8. Condition of combustion:

A rich mixture or a stoichiometric mixture will not give  $\text{SO}_3$  during combustion.

9. Air fuel ratio:

Air fuel ratio to be maintained constant during sampling. Constant watch on rotameter floats was necessary to check any change in air fuel flow rates.

10. Cleanliness of condenser filter and probe:

Deposits of acid, alkali or any other foreign matter in the condenser, filter or probe could effect the minute quantity of  $\text{SO}_3$ . All the above items and other washing items like conical flasks, etc to be thoroughly washed by acetone and dried every time before usage.

11. pH of washing solution:

pH of washing solution must be 4.6, every time before washing the condensate the pH of the solution to be checked and if necessary corrected.

12. Strength of NaOH:

The strength of NaOH used was 0.2 N. This could be checked by adding a few drops of indicator to a measured quantity of NaOH and titrating with the same strength of  $H_2SO_4$ .

Requirement of the same quantity of  $H_2SO_4$  to reach end point proves the strength of NaOH to be 0.2 N.  $SO_3$  value is calculated by using the following equation determined by Goksoyer and Ross

$$SO_3 = \frac{T \times N \times 11.2 \times 10^6}{V \times 10^3}$$

Hence a variation in the strength (N) of NaOH could effect the value of  $SO_3$ .

13. Amount of NaOH used for titration:

The titration value of NaOH should be accurate. Titration should stop when end point is reached. Hence, determination of end point is important.

14. Quantity of washing solution:

The quantity of washing up solution used for washing condensate should be exactly the same in all cases (50 ml).

15. Amount of gases sampled:

The amount of gases sampled should be exactly 100 liters during each sampling.

16. Position of sampling probe:

The sampling probe has to be positioned at the centre of the combustion tube. In laminar flow conditions the velocity and the gas temperature will be maximum at the centre.

17. Rate of sampling:

Sampling should be done isokinetically, ie, the gas velocity in the tube and the sampling probe should be equal so that the flow pattern is not disturbed.

APPENDIX IX

RADIATION CORRECTION OF TEMPERATURE MEASURED BY FINE WIRE  
THERMOCOUPLE

Data:

Thermocouple material - platinum/13% rhodium-platinum

Thermocouple bead diameter (d) -  $70\mu\text{m}$

Thermocouple indicated temperature ( $T_T$ )  $726^\circ\text{C}$  -  $999\text{K}$

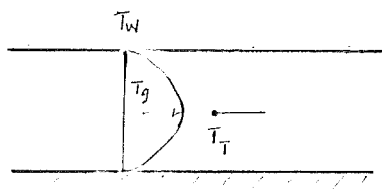
Combustor wall temperature ( $T_N$ ) -  $648^\circ\text{C}$  -  $921\text{K}$

Emissivity (E) of thermocouple material - 0.1480.

Flue gas velocity at  $726^\circ\text{C}$  =  $1.9\text{ ms}^{-1}$  (calculated).

It is assumed that combustion gases behave like air at high temperatures. Hence, property values of air are used in these calculations.

As we do not know the exact gas temperature we may use its property values at  $999\text{K}$ .



$T_w$  - wall temperature

$T_g$  - actual gas temperature

$T_T$  - thermocouple indicated temperature

From Bradley and Mathews (37)

The heat transfer co-efficient (h) can be found from

$$\text{Nu} = 0.42 \text{Pr}^{0.2} + 0.57 \text{Pr}^{0.33} \times \text{Re}^{0.5}$$

$$\text{where } Nu = \frac{hd}{k} \quad \text{and } Re = \frac{Vd}{\Delta}$$

$$K - \text{Thermal conductivity} = 6.754 \times 10^{-5} \text{ KWM}^{-2} \text{ K}^{-1} \text{ at } 1000\text{K}$$

$$\Delta - \text{Kinematic viscosity} = 11.76 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$$

$$Pr - \text{Prandtl no} = 0.702$$

(The above values were from Thermodynamic transport properties. By Rogers and Mayhew Page 16).

$$\frac{hd}{k} = 0.42 Pr^{0.2} \times 0.57 Pr^{0.33} \times \left(\frac{Vd}{\Delta}\right)^{0.5}$$

$$\frac{h \times 70 \times 10^{-6}}{6.754 \times 10^{-5}} = 0.42(0.702)^{0.2} + 0.57(0.702)^{0.33} \left(\frac{1.9 \times 70 \times 10^{-6}}{11.76 \times 10^{-5}}\right)^{0.5}$$

$$h = 0.8973$$

From energy balance ignoring conduction heat loss as this will be negligible.

Heat gained by convection = Heat lost by radiation.

$$hA(T_g - T_T) = EG(T_T^4 - T_w^4)$$

where G - Stefan Boltzman constant  $56.7 \times 10^{-12} \text{ KWM}^{-2} \text{ K}^{-4}$

A - Area of thermocouple

$$\therefore h(T_g - T_T) = EG(T_T^4 - T_w^4)$$

$$T_g = EG \frac{(T_T^4 - T_w^4)}{h} + T_T$$

$$= \frac{0.148 \times 56.7 \times 10^{-12} (999^4 - 921^4)}{.8973} + 999$$

$$= 1001.59$$

$$T_g = 1002 \text{ K}$$

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∴ Actual gas temperature = 1002 K

∴ The percentage error in this  
temperature measurement = -0.41%

APPENDIX XI

CALCULATION OF THE VELOCITY OF COMBUSTION GASES AT 550°C

Fuel consumption	6 cc/min
density of fuel Kerosene	0.783 g/cc
internal diameter of combustion tube	= 76 mm
O <sub>2</sub> % in flue gas	4.5

1 kg of kerosene when burnt at NTP will produce  
12.13 m<sup>3</sup> combustion gases during stoichiometric combustion  
(46)

∴ combustion gases produced when burnt 6 cc/min  
kerosene =  $6 \times 10^{-3} \times .783 \times 12.13 \text{ m}^3/\text{min NTP}$   
=  $56.98 \times 10^{-3} \text{ m}^3 \text{ min}^{-1} \text{ NTP}$

Theoretical combustion air required for burning  
1 kg of kerosene at NTP = 11.35 m<sup>3</sup> (46)  
for 4.5% excess O<sub>2</sub> in combustion gases 22% excess air  
is needed.

∴ Amount of excess air used per kg of fuel  
$$= 11.35 \times \frac{22}{100} = 2.5 \text{ m}^3 \text{ NTP}$$

∴ Amount of excess air used during combustion of  
6 cc min<sup>-1</sup> fuel =  $2.5 \times 6 \times 10^{-3} \times .783$   
=  $11.745 \times 10^{-3} \text{ m}^3 \text{ min}^{-1} \text{ NTP}$

∴ Total volume of combustion gases produced using 22%  
excess air =  $(56.98 \times 10^{-3} + 11.75 \times 10^{-3}) \text{ m}^3 \text{ min}^{-1} \text{ NTP}$   
=  $68.73 \times 10^{-3} \text{ m}^3 \text{ min}^{-1} \text{ NTP}$

It is assumed the pressure change in the system is negligible.

∴ volume of combustion gases at 550°C

$$\begin{aligned} \frac{V_2}{V_1} &= \frac{T_2}{T_1} = 68.73 \times \frac{823}{273} \times 10^{-3} \\ &= 207.2 \times 10^{-3} \text{ m}^3 \text{ min}^{-1} \end{aligned}$$

$$\text{cross-area of combustion tube} = \frac{\pi \times (76)^2 \times 10^{-6}}{4}$$

$$= 45.36 \times 10^{-4} \text{ m}^2$$

$$\begin{aligned} \therefore \text{mean velocity of gases at } 550^\circ\text{C} &= \frac{207.2 \times 10^{-3} \text{ ms}^{-1}}{45.36 \times 10^{-4} \times 60} \\ &= 0.76 \text{ ms}^{-1} \end{aligned}$$

The flow of combustion gases in the tube was laminar  
(Appendix IV)

Since the flow is laminar, the maximum velocity of gas will be in the centre of the tube and will be twice the mean velocity (47) if the flow is fully developed.

∴ The maximum velocity of gases at 550°C = 1.52 ms<sup>-1</sup>



APPENDIX XII

COURSES AND CONFERENCES ATTENDED AND  
PUBLICATIONS DURING THE PRESENT PERIOD OF STUDY

COURSE

COMBUSTION FUNDAMENTALS

IMPERIAL COLLEGE, LONDON      JUNE 1985

CONFERENCES

SULPHUR COMPOUNDS AND COMBUSTION

COMBUSTION INSTITUTE AUTUMN MEETING

UMIST                              OCT 1985

PUBLICATION

THIS PAPER IS ENCLOSED IN A FLAP AT THE END OF THIS THESIS

"THE INFLUENCE OF HIGH TEMPERATURE AND RESIDENCE TIME ON

THE FORMATION OF  $\text{SO}_3$  IN A PREMIXED LAMINAR FLAME"

JOURNAL OF THE INSTITUTE OF ENERGY

JUNE 1988.

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